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APPARATUS AND METHODS FOR INVESTIGATING THE CHEMICAL CONSTITUTION OF LUBRICATING OIL, AND PRELIMINARY FRACTIONATION OF THE LUBRICATING-OIL FRACTION OF A MIDCONTINENT PETROLEUM [1]

By Beveridge J. Mair,[2] Sylvester T. Schicktanz,[2] and Frank W. Rose, Jr.[2]

ABSTRACT

In the fall of 1933 work on American Petroleum Institute Research Project 6 at the National Bureau of Standards, which up to that time had been confined to the naphtha fraction of petroleum, was extended to include the lubricating oil fraction. This paper gives the first report on the apparatus and methods developed for investigating the chemical constitution of lubricating oil and describes the preliminary separation of the lubricant fraction of a midcontinent petroleum into "wax", "extract", and "water-white" fractions by dewaxing with ethylene chloride, extracting with sulphur dioxide, and filtering through silica gel. The results of the first four stages of distillation of the water-white oil are given.

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I. INTRODUCTION

Researches on the chemical constitution of the lubricant fraction of petroleum have been going on for more than 30 years. In these investigations usually one, or at the most two, methods of fractionation have been used, and these not exhaustively. The available information indicates that the average molecular formulas of fractions of lubricating oils range from about C_nH_{2n} to about C_nH_{2n-20}. In some cases fractions even poorer in hydrogen have been obtained.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

The low ratio of hydrogen to carbon in these oils is attributed not to unsaturation, as in olefinic hydrocarbons, but rather to the existence in the molecule of one or more naphthenic (saturated) ring nuclei, as in cyclopentane and cyclohexane, or aromatic ring nuclei as in naphthalene and anthracene, etc. The extent of our present actual knowledge of the chemical constituents of lubricating oil may be summed up in the statement that from it not one pure hydrocarbon has ever been isolated.

Modern demands in the automotive field for lubricants having good lubricity or oiliness, high resistance to oxidation and decomposition, a low temperature coefficient of viscosity, and a low congealing temperature have made it very desirable that something definite be learned about the hydrocarbon constituents of lubricating oil. Consequently, the work on American Petroleum Institute Research Project 6 at the National Bureau of Standards, which up to the fall of 1933 had been confined to the naphtha fraction of petroleum, was extended to include the lubricating oil fraction. The purpose of the present investigation is to separate the lubricant fraction exhaustively by all feasible physical processes, such as distillation, crystallization, solvent extraction, and selective adsorption, in the hope that there may be isolated individual hydrocarbons, or at least hydrocarbons of a single type and nearly equal molecular weights.

This paper presents a description of the apparatus and methods used, and the results of the preliminary separation of a midcontinent petroleum into wax, extract, and water-white fractions, together with the results of the first four stages of the distillation of the last.

II. SOURCE OF THE LUBRICATING-OIL FRACTIONS

The lubricating oil came from the same 1,000-gallon lot of crude petroleum from well no. 6 of the South Ponca Field, Kay County, Okla., as did the naphtha distillate which is under investigation in this laboratory.[3] [4] Before receipt at this Bureau, the portion of the crude petroleum containing the lubricating oil was fractionally distilled in "vacuo" by the Sun Oil Co., at Philadelphia. The fractions (of about 1¼ to 1½ gallons each) were shipped in tightly sealed metal containers, from which the air had been displaced by nitrogen. Sixteen of these fractions (designated as cuts 23 to 38), with a total weight of about 67 kg and representing 10 percent of the crude oil, had a sufficiently high viscosity to be of interest in this investigation.

III. EXTRACTION WITH LIQUID SULPHUR DIOXIDE

The first steps in the preparation of an oil free from wax, and from asphaltic and resinous materials, were crystallization from ethylene chloride to remove the wax and extraction with liquid sulphur dioxide to remove asphaltic and resinous materials. Cuts 23 to 29, inclusive, were extracted before dewaxing. Because of the high-melting nature of the waxes in cuts 30 to 38, it was found preferable to dewax them before extracting with sulphur dioxide.

Four extractions were performed on each cut. In the first extraction the ratio by weight of sulphur dioxide to oil was 7 to 9, while

[3] See figure 1, Leslie and White [1].

[4] The figure in brackets in footnote 3 and elsewhere in this paper refer to the numbered literature references given on page 573.

in the last three the ratio was 5 to 9. The apparatus used for this extraction is shown in figure 1. It consisted essentially of the metal cylinder A, in which the mixing of the lubricating oil with sulphur dioxide took place, the liter distilling flask E, into which the extract first flowed from the mixing cylinder, a second flask G (5-liter capacity), into which the extract was then forced, and from which the sulphur dioxide was distilled through the drying tower D into the condenser J,

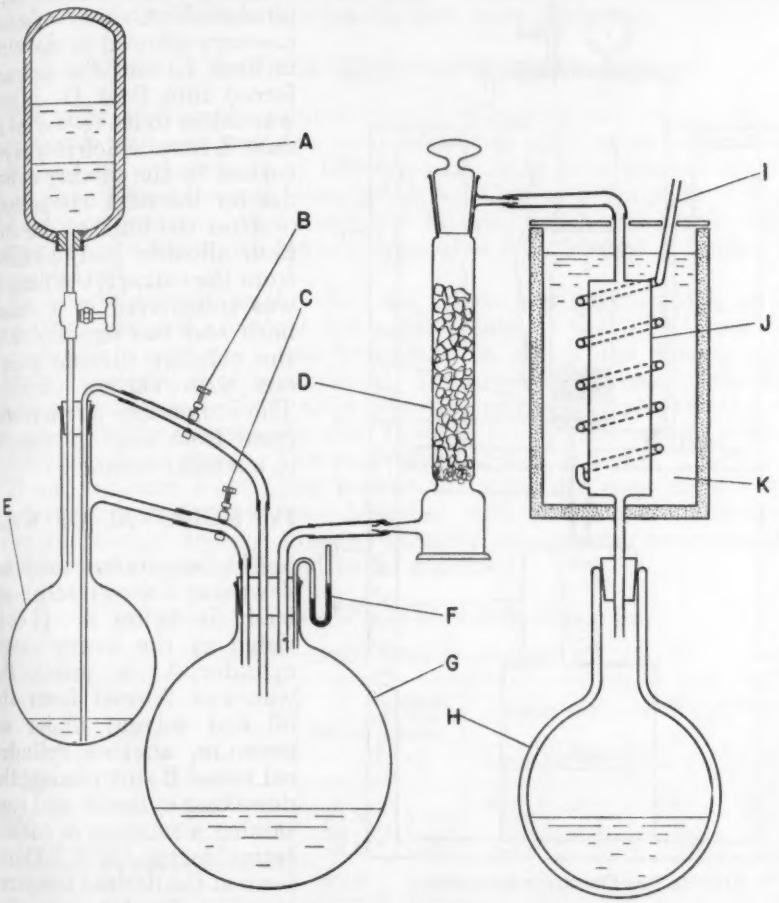

FIGURE 1.—*Extraction apparatus.*

and collected in the dewar flask H. To avoid the blowing out of stoppers, the pressure in G, observed on the manometer F, was not allowed to exceed about 2 cm of mercury. I is a vent from the bottom of the condenser to the atmosphere. K is an insulated metal container. It held the refrigerant, a mixture of chloroform and carbon tetrachloride chilled with solid carbon dioxide.

For extraction, the mixing cylinder containing a weighed quantity of oil was chilled with solid carbon dioxide and the required amount of sulphur dioxide introduced. The outlet valve was replaced in the cylinder and the cylinder warmed to about 45° C and shaken vigor-

ously. The cylinder was placed in position above the distilling flask E and the valve opened slightly. The pressure exerted by the sulphur dioxide forced the extract out rapidly. Oil was always observed floating on the surface of the extract in the distilling flask. Some of this oil came through the valve before the operator could observe the change in phase of the liquid and close the valve. Most of it was probably due to precipitation of constituents of the extract as it refrigerated itself. The pinchcock C was closed, pressure allowed to develop in flask E, and the extract forced into flask G. Care was taken to leave the oil in flask E from which it was returned to the mixing cylinder for the next extraction.

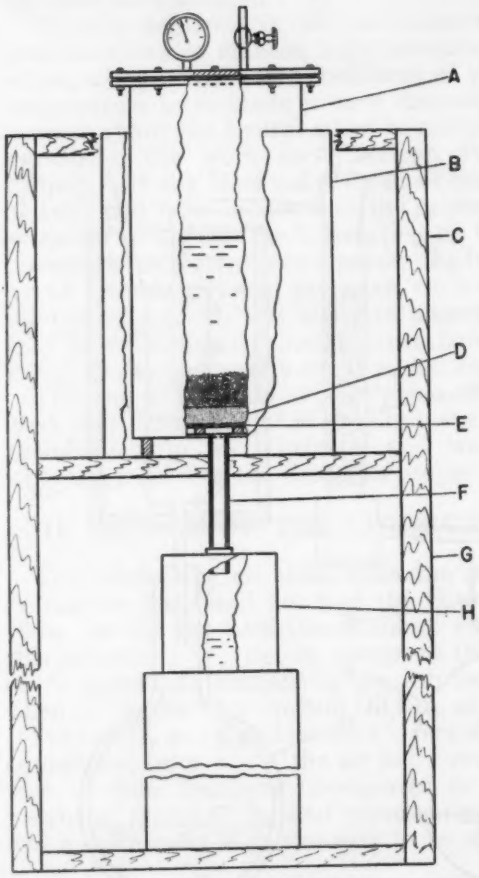

FIGURE 2.—*Dewaxing apparatus.*

After the bulk of the sulphur dioxide had distilled from the extract, the flask G was transferred to a steam bath and the remainder of the sulphur dioxide swept out with carbon dioxide. The immiscible portion was freed from sulphur dioxide in a similar manner.

IV. REMOVAL OF WAX

The apparatus used for dewaxing is shown schematically in figure 2. It consisted of the heavy metal cylinder A, in which the wax was filtered from the oil and solvent under air pressure, another cylindrical vessel B surrounding the dewaxing cylinder and containing a mixture of carbon tetrachloride and chloroform at the desired temperature, an insulated wooden box C, which was raised from the floor on legs G and which held the dewaxing cylinder. F is a tube which was soldered to the bottom of the dewaxing cylinder and through which oil and solvent flowed to the receiving vessel H. The lid of the dewaxing cylinder contained a pressure gage and a valve through which pressure was applied to the cylinder. When filtering, the lid was bolted to a flange on the upper periphery of the cylinder and sealed tightly with a leather gasket. Fitting snugly inside the filtering cylinder and supported on short legs about 1 cm from the bottom was the perforated circular brass plate E. Over this, fitting the walls of the cylinder tightly, was placed the disk of felt D, about 2 cm thick, which served as a filtering medium.

In dewaxing, the oil, mixed with four times its volume of ethylene chloride, was warmed to dissolve the wax, then cooled slowly to −18° C and the wax removed by filtration under air pressure of 50 lb/in.[2] The wax was then recrystallized from ethylene chloride and filtered again under pressure. The bulk of ethylene chloride was distilled from the mother liquors. The last of the solvent was removed from both the oil and wax by sweeping it out at 110° C with a strong stream of carbon dioxide gas. Tests of the dewaxed oil for chlorides indicated that chlorination had been negligible.

V. FILTRATION THROUGH SILICA GEL

The raffinate from the sulphur dioxide extraction contained sulphur compounds and was unstable with respect to color when exposed to light and air. A sample of this oil, containing 0.14 percent of sulphur, was filtered through silica gel at 90° C in an attempt to reduce the sulphur content. A water-white filtrate, which was stable with respect to color and which contained less than 0.01 percent of sulphur[5], was obtained.

To ascertain whether the silica gel cracked or polymerized, or in any other manner attacked the constituents of the lubricating oil fraction, an experiment was performed in which the filtrate and adsorbed material were recombined. The results of this experiment which are given in table 1, show that the physical characteristics of the combined fractions agree with those of the original sample within the experimental error. The recovery was 99.9 percent.

It also appears from table 1 that the silica gel does more than remove sulphur compounds. Material with the higher refractive index and higher density, greater viscosity, and greater temperature coefficient of viscosity tended to be adsorbed.

TABLE 1.—*Nature of adsorption with silica gel*

[Oil passed through 102 g of silica gel at 90 to 100° C]

Material	Weight	Refractive index, n_D^{25}	Density at—		Kinematic viscosity at—	
			150° F	210° F	150° F	210° F
	g		g/ml	g/ml	*Stoke*	*Stoke*
Original	311.58	1.4710	0.846	0.824	0.1360	0.0565
Filtrate	246.44	1.4663	.838	.815	.1245	.0540
Adsorbed material [1]	64.83	1.4899	.875	.851	.1710	.0653
Recombination of filtrate with adsorbed material	311.27	1.4710	.846	.825	.1361	.0565

[1] Recovered from the gel by washing with ethylene chloride and acetone.

It has been shown in this laboratory [2] that aromatic hydrocarbons may be completely removed from the naphtha distillate of petroleum by adsorption on silica gel. It seems probable that aromatic hydrocarbons also were adsorbed from the lubricating oil, and possibly to a small extent naphthenes.

Since it had been determined in the preceding experiments that treatment with silica gel removed sulphur compounds and gave a water-white oil which did not darken on exposure to light and air, and also that the gel itself did not harm the oil appreciably, it was

[5] The sulphur determinations were made by C. E. Waters of this Bureau.

decided to remove sulphur compounds from all the fractions by means of silica gel and obtain a stable oil for further work.

Glass tubes mounted vertically served to hold the gel. These tubes were 150 cm long and 2 cm in internal diameter and held about 280 g of gel. Silica gel of grade "150–F–850" (40 to 200 sieve), obtained from the Silica Gel Corporation, of Baltimore, was used. The procedure finally adopted was to mix the oil with from 1 to 3 times its volume of petroleum ether, depending on its viscosity, pour it onto the gel, and allow it to filter at room temperature under gravity.

The first portion of the filtrate was water-white, and then yellow and darker fractions came through. Oil was added to the top of the column and allowed to filter until the color of the filtrate was almost

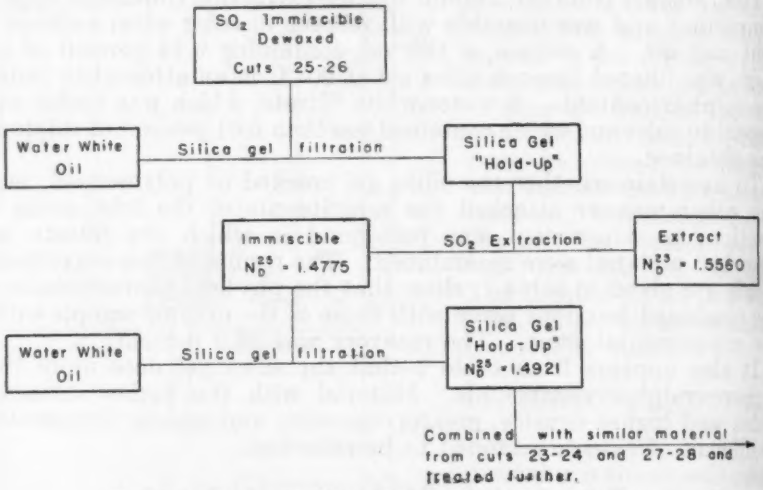

FIGURE 3.—*Interlocking of extraction with adsorption.*

as dark as that of the oil added. The water-white filtrate was stored separately, the colored fractions were poured onto fresh columns of gel in order of their color, and further water-white fractions were obtained. The oil held on the gel was washed off by adding ethylene chloride to the top of the column, allowing it to filter through, and draining it with suction. This treatment was repeated several times. Finally, a small amount of material which was not readily removed with ethylene chloride was washed off with acetone. The bulk of the solvents was distilled off on the steam bath, and the remainder swept out by passage of a rapid stream of carbon dioxide gas. The oil recovered from the gel with ethylene chloride and acetone contained not only that portion of the oil actually adsorbed by the gel but also a portion of the oil which was retained between the particles by surface tension, much of which could be rendered water-white. To obtain from the material held on the gel a further quantity of water-white oil, an interlocking process of extraction with sulphur dioxide and adsorption with silica gel was employed. The first steps of this interlocking process are shown schematically in figure 3 for cuts 25-26.

When the quantity of silica gel "hold up" from cuts 25-26 became too small to be handled satisfactorily, it was mixed with the corresponding hold up from cuts 27-28, and 23-24, and the treatment continued.

TABLE 2.—*Physical properties of original oil, wax, sulphur dioxide extract, and water-white oil*

TABLE 2.—*Physical properties of original oil, wax, sulphur dioxide extract, and water-white oil*

Cut	Original oil				Wax (total weight 20.25 kg)				Sulphur dioxide extract (total weight 17.93 kg)				Water-white oil (total weight 19.78 kg)					
	Kinematic viscosity at—		Density at—		Kinematic viscosity at—		Density at—		Kinematic viscosity at—		Density at—		Kinematic viscosity at—		Density at—		Refractive index	Weight
	150° F	210° F	150° F	210° F	150° F	210° F	150° F	210° F	100° F	210° F	100° F	210° F	100° F	210° F	100° F	210° F	n_D^{23}	
	Stoke	*Stoke*	g/ml	g/ml	*Stoke*	*Stoke*	g/ml	g/ml	*Stoke*	*Stoke*	g/ml	g/ml	*Stoke*	*Stoke*	g/ml	g/ml		g
23	0.094	0.0460	0.854	0.835	0.0615	0.0330	0.783	0.761	1.89	0.0807	0.989	0.948	0.214	0.0422	0.849	0.804	1.4684	3,134
24	.103	.0452	.856	.836	.0705	.0354	.794	.773	1.72	.0828	.987	.963						
25	.113	.0480	.858	.837	.0735	.0379	.799	.779	2.60	.0915	.983	.950	.257	.0465	.847	.082	1.4704	2,512
26	.119	.0523	.859	.839	.0825	.0400	.800	.780	2.72	0942	.983	.956						
27	.128	.0536	.860	.840	.0822	.0410	.800	.781	4.12	.113	.992	.958	.300	.0498	.850	.809	1.4709	2,944
28	.138	.0575	.862	.842	.0893	.0473	.805	.784	4.57	.125	.991	.955						
29	.138	.0583	.863	.843	.0902	.0518	.805	.786	6.79	.137	1.013	.982	.328	.0547	.850	.821	1.4733	2,189
30	.143	.0588	.859	.839	.0925	.0457	.804	.783	3.37	.118	.971	.932						
31	.176	.0687	.865	.844	.104	.0498	.813	.792	191	.359	1.067	.990	.409	.0604	.857	.831	1.4739	2,214
32	.213	.0828	.870	.850	.118	.0555	.812	.792										
33	.256	.104	.873	.856	.131	.0777	.819	.799	28.5	.268	.993	.950	.591	.0785	.856	.819	1.4743	1,608
34	.311	.108	.877	.857	.173	.0736	.826	.806										
35	.329	.114	.879	.859	.187	.0785	.829	.810	64.7	.383	1.007	.960	.757	.0882	.860	.825	1.4771	958
36	.446	.146	.884	.865	.....	.0835	.....	807										
37	.557	.160	.886	.867	.....	.0976	.....	.817	384	.712	1.032	.970	.824	.0952	.862	.825	1.4772	505
38	.648	.187	.891	.870	.....	.1102	.....	.818										
a [1]	.....	.....	.....	.....	.....	.....	.....	.....	2.80	.122	.972	.955	.605	.0715	.878	.841	1.4909	1,423
b [1]	.....	.....	.....	.....	.....	.....	.....	.....	6.60	.187	.967	.936	.584	.0769	.866	.826	1.4815	595
c [1]	.....	.....	.....	.....	.....	.....	.....	.....	8.78	.255	.949	.912	1.13	.1096	.873	.845	1.4861	1,693

[1] a, b, and c are from silica gel hold up of cuts 23-28, 29-32, and 33-38, respectively. (See text and fig. 3.).

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In table 2 are shown certain physical characteristics of the original oil, wax, sulphur dioxide extract, and water-white oil fractions obtained by the processes just described. A total of 19.78 kg of water-white oil was obtained. Most of this oil had a viscosity-temperature relationship similar to that of a refined Pennsylvania oil. The viscosity indices [3] for the various fractions ranged as follows: Original oil, about 75 to 90; wax, about 125 to 150; extract, about −150 to −300; water-white, about 100 to 120.

VI. DISTILLING EQUIPMENT

The design of distilling equipment is limited by the low vapor pressures of these oils at any temperature below that at which thermal decomposition begins. Two types of stills were used: Short fractionating columns for the more volatile portion of the oil and molecular stills for the less volatile portion.

1. FRACTIONATING COLUMNS

One of the fractionating columns is shown in figure 4. It consisted of a Pyrex flask E, which served as a still pot into which the oil was charged through the side tube I. The still was sealed to a tube 120 cm long and 2 cm in inside diameter which served as the column. At the top of the column was sealed a bulb A, which served as a condenser and from which the distillate passed through the tube B to the receiver. This receiver was so designed that fractions could be withdrawn without breaking the vacuum in the still proper.

The high-vacuum line was sealed to B and led to the liquid-air trap F and to the McLeod gage and mercury-diffusion pump. Surrounding the column itself, and concentric with it, was a large glass tube D equipped for electrical heating and insulated with about 1 cm of asbestos. The still pot, placed in a metal container, was insulated with asbestos and heated electrically. Since the pressure in the pot E, and consequently the temperature, depend on the resistance to flow encountered by the vapors in their passage from E to A, the only packing used in this column was a spiral of no. 8 copper wire. This spiral fitted the walls of the column closely and, although offering little resistance to passage of the vapors, retarded the return of the reflux and spread it more uniformly over the entire surface of the column. All stoppers and stopcocks were lubricated with tetraethylene glycol citrate resin. With this excellent lubricant [4] which is insoluble in oils, little difficulty was experienced with leaks, the stopcock seals remained good during many charges of the still.

The still was operated with a large reflux in comparison to the amount of distillate. Heat was applied to the column so that the amount of reflux appeared to be about the same throughout its length. The rate of distillation was about 0.5 ml per minute. To avoid thermal decomposition of the oil, the use of this type of column was confined to oils which could be distilled without the still-pot temperature rising above 250° C. Temperatures in the still pot of 250° C were reached in the distillation of oils having a viscosity of about 0.6 stoke (about 280 Saybolt) at 100° F. The temperatures in the still head ranged from about 160 to 190° C. A pressure of 10^{-4} mm of Hg or lower (observed on the McLeod gage) was readily maintained throughout the distillations without the continuous use of the fore

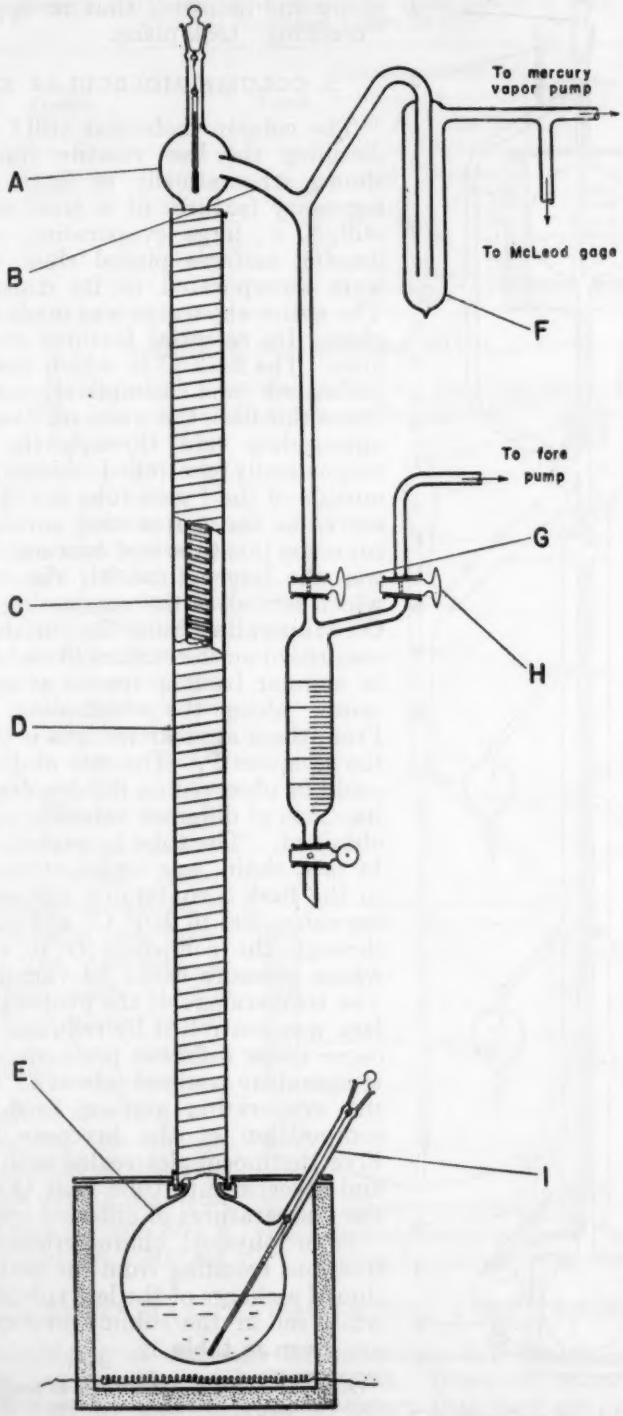

FIGURE 4.—*Vacuum fractionating column.*

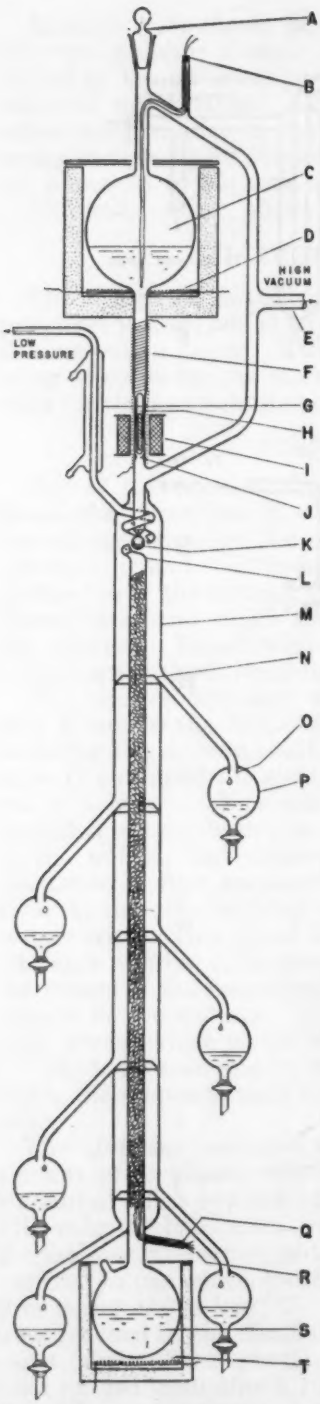

FIG. 5.—*Column molecular still.*

pump and indicated that no appreciable "cracking" took place.

2. COLUMN MOLECULAR STILL

The column molecular still [6] used for distilling the less volatile fractions is shown schematically in figure 5. The necessary features of a good molecular still, i. e., large evaporating and condensing surfaces placed close together, were incorporated in its construction. The entire apparatus was made of Pyrex glass. Its essential features are as follows. The flask C in which the oil was preheated and completely degassed. From this flask the warm oil flowed at an appropriate rate through the electromagnetically controlled valve H to the outside of the Pyrex tube L. This tube served as the evaporating surface. Surrounding this tube and concentric with it was the larger tube M, the inside of which served as the condensing surface. Oil evaporating from the surface L was condensed on the surface M and collected in annular troughs spaced at equal distances along the condensing surface. From these annular troughs it passed to the receivers P. The rate of distillation could be observed on the drippers O. Six fractions of different volatility were thus obtained. The tube L, packed with no. 14 jack chain, was sealed at the bottom to the flask S containing kerosene (boiling range 200 to 250° C) and at the top through the condenser G to a system whose pressure could be varied at will. The temperature of the evaporating surface was controlled by refluxing the kerosene under different pressures, and the temperature gradient (about 15° C) along the evaporating surface fixed by the composition of the kerosene mixture. Five thermocouples sealed with litharge and glycerin into tube L at Q recorded the temperatures of different sections.

Some physical characteristics of the fractions resulting from the first distillation of a charge of the less volatile water-white oil in the column molecular still are given in table 3.

[6] Since the construction of this still we have learned that similar stills have been used for some time by W. H. Bahlke, of the Standard Oil Co., of Ind.

TABLE 3.—*Properties of fractions resulting from distillation of a charge of water-white oil in column molecular still*

Fraction	Weight	Kinematic viscosity at—		Refractive index n_D^{25}	Temperature of section of still
		100° F	210° F		
	g	*Stoke*	*Stoke*		°C
Original	900	1.134	0.1096	1.4861	
1	219	.650	.0747	1.4840	214
2	202	.966	.0967	1.4852	214
3	150	1.321	.1171	1.4860	214
4	117	1.650	.1351	1.4867	218
5	84	1.987	.1537	1.4875	228
Residue	127	3.067	.2165	1.4901	

3. SIMPLE MOLECULAR STILL

Simple molecular stills were also useful for distilling the less volatile fractions. The best type of simple molecular still tried is the one depicted in figure 6. This still [7] consisted of the large Pyrex-glass cylinder E sealed at the bottom, and drawn down and sealed at the top to the smaller tube A used for introducing the charge and withdrawing the residue. Attachment to the high-vacuum system was also made through this tube. The distillate which condensed on the surface B was caught in the annular trough C and flowed through the side arm D to a multiple receiver. A small funnel with iron core, operated electromagnetically, was used to direct the distillate as desired into each of the six small receivers which constituted the multiple receiver. The vacuum was not broken during the distillation of the charge. Molecular stills of this type were made with a diameter up to about 12 cm and a capacity of about 1,500 ml.

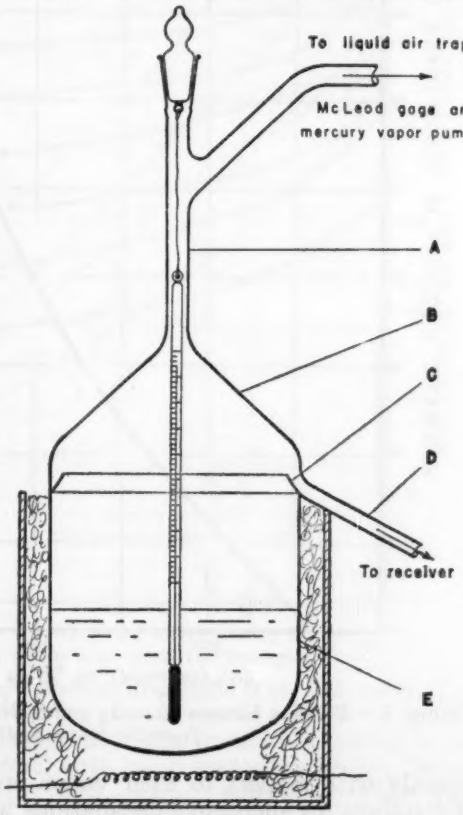

FIGURE 6.—*Simple molecular still.*

VIII. SYSTEMATIC FRACTIONAL DISTILLATION

The combining of fractions for successive distillations is usually based on the property of boiling point. However, other physical properties may be used if it can be shown that they are continuous

[7] Stills similar to this have been described by Hickman and Sanford [5].

functions of the boiling point. Owing to the low vapor pressure of these fractions, the accurate determination of their boiling points is a time-consuming process, and blending on the basis of some property more easily determinable is desirable. There was a continuous increase in the viscosity of the fractions of water-white oil with respect to the order in which they were removed from the still and conse-

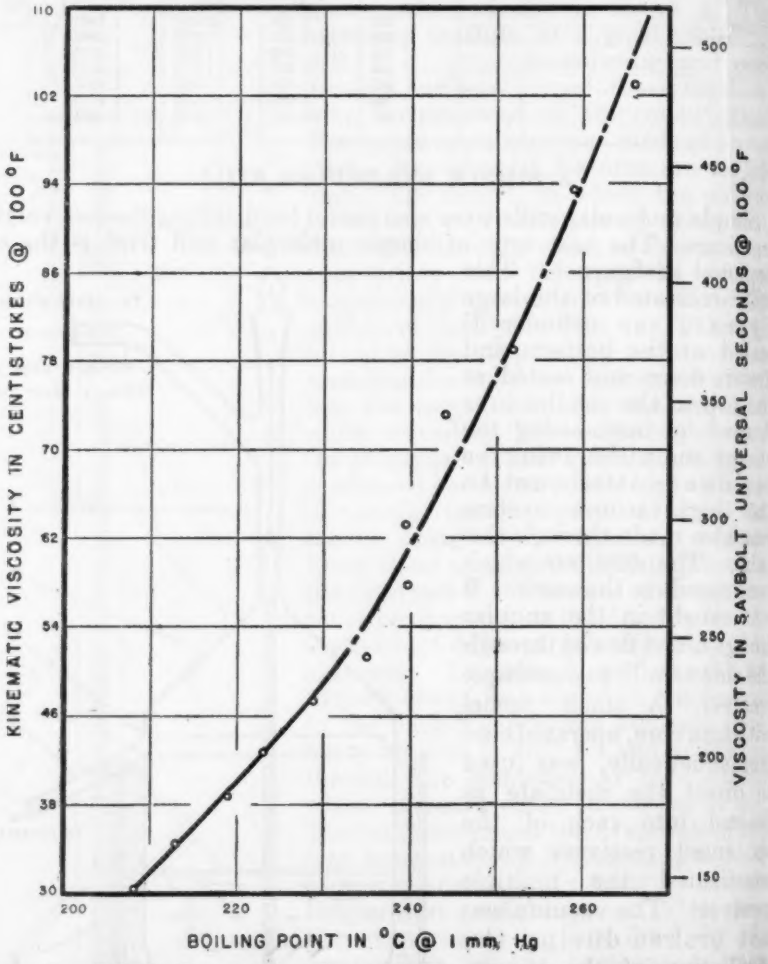

FIGURE 7.—*Relation between viscosity and boiling point of water-white oil fractions from the fourth distillation.*

quently with respect to their vapor pressures. Therefore, blending of fractions for successive distillations was accomplished on the basis of viscosity (instead of boiling point). In figure 7 is shown a plot of the viscosity with respect to the boiling point [8] at 1-mm pressure obtained on some of the fractions resulting from the fourth distillation. It is apparent that the viscosity increases continuously with increase in boiling point. This relationship between viscosity and boiling

[8] The apparatus used for the boiling-point determinations has been described by Schicktanz [6].

point may be expected to break down if one type of hydrocarbon is concentrated within a narrow boiling range during distillation. However, there is no evidence that any such concentration has occurred at this stage of the distillation.

What has been accomplished by the systematic fractional distillation of the more volatile portion of water-white oil is shown in figure 8, in which are plotted the viscosities of the fractions with respect to

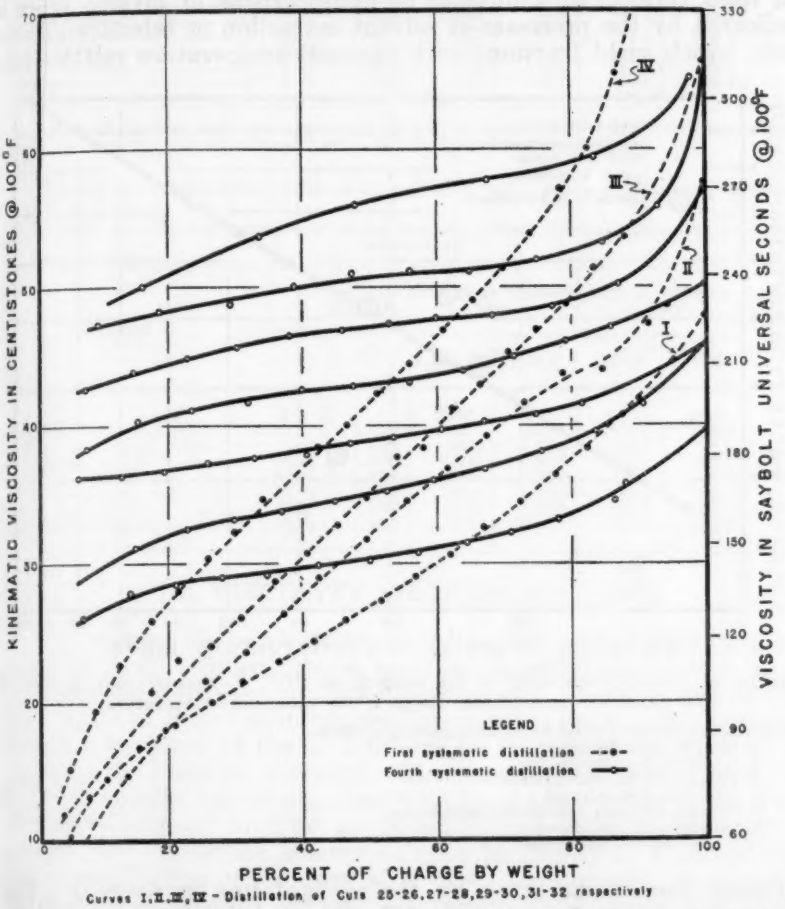

FIGURE 8.—*Result of four stages of systematic distillation of the water-white oil.*

the percentage by weight of the charge. The fractions resulting from the first distillation of the original cuts (represented by broken lines) cover a wide range in viscosity and overlap markedly, while the fractions resulting from the fourth distillation (represented by solid lines) cover a much smaller range in viscosity and show comparatively little overlapping.

At the end of the fourth distillation the total quantity of water-white oil in the region under investigation (viscosity, 140 to 500 Saybolt seconds) was 10.7 kg, of which about 6.5 kg lay in the region from 140 to 280 Saybolt seconds.

In figure 9 a plot on a logarithmic scale of the viscosity at 210° F with respect to that at 100° F for a large number of distillation fractions is shown together with values for the viscosities of several synthetic hydrocarbons.[9] The data for successive distillations may be reproduced within the experimental error by a straight line. This is taken to indicate that no appreciable concentration of hydrocarbons by type has resulted from fractional distillation. That the oil itself consists of a mixture of hydrocarbons of diverse types is indicated by the processes of solvent extraction or selective adsorption, which yield fractions with viscosity-temperature relationships

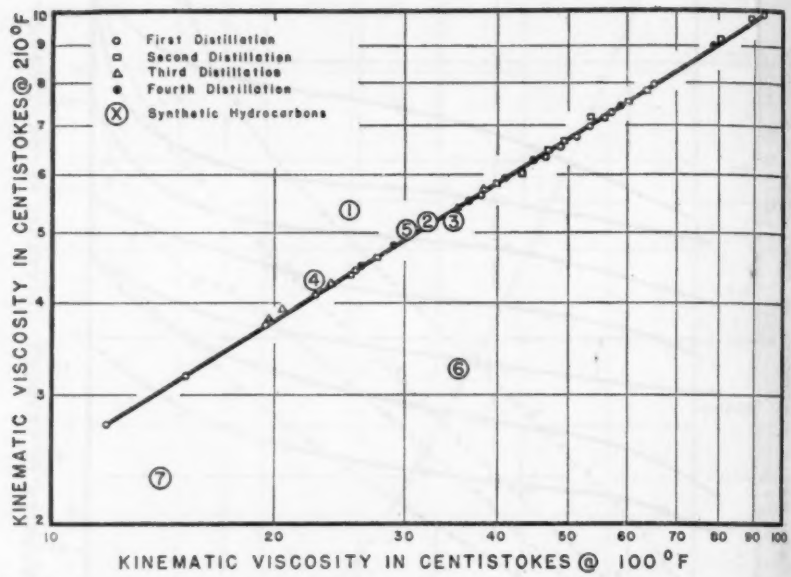

FIGURE 9.—*Logarithmic scale of the viscosity at 210° F against that at 100° F for fractions from various stages of the systematic distillation.*

The numbers represent values for the hydrocarbons as follows:

1. 16-*n*-Butylhentriacontane.
2. 1, 1-Dicyclohexylhexadecane.
3. 1-Phenyl-2-benzylheptadecane.
4. 1, 1-Diphenylhexadecane.
5. 1-Cyclohexyl-2-hexahydrobenzylheptadecane.
6. Dihydrodiethylanthracene.
7. 1, 4-Diisobutylnaphthalene.

different from those given by the straight line in figure 9. This separation into fractions with different viscosity-temperature relationships by solvent extraction is shown by the data in table 4, in which are recorded certain physical properties of fractions resulting from extraction of a distillation fraction with acetone. Similarly certain physical properties of fractions resulting from adsorption of a distillation fraction on silica gel are recorded in table 5. It is evident that here also a separation with respect to type has occurred.

[9] The values for the synthetic hydrocarbons were obtained by interpolation or extrapolation with the aid of Cragoe's [7] equation from the original data, which extended from approximately 20 to nearly 100° C, of Suida and Planckh [8] for 16-n-butylhentriacontane, Landa and Cech [9] for 1, 1-dicyclohexylhexadecane, 1-phenyl-2-benzylheptadecane, 1, 1-diphenylhexadecane, 1-cyclohexyl-2-hexahydrobenzylheptadecane, Lerer [10] for dihydrodiethylanthracene, and 1, 4-diisobutylnaphthalene.

TABLE 4.—*Extraction, with acetone, of a water-white distillation fraction*

Fraction	Weight	Refractive index n_D^{25}	Kinematic viscosity at—		Saybolt universal viscosity [1] at—		Viscosity index
			100° F	210° F	100° F	210° F	
	Percent		*Stoke*	*Stoke*	sec	sec	
Original	100	1.4728	0.3693	0.0546	172.1	43.4	93
First extract	12.17	1.4764	.4174	.0582	194.1	44.5	87
Second extract	12.42	1.4746	.4027	.0578	187.5	44.3	93
Third extract	27.85	1.4722	.3766	.0557	175.5	43.7	94
Fourth extract	27.51	1.4705	.3596	.0548	167.7	43.4	97
Raffinate	20.05	1.4682	.3343	.0546	156.3	43.4	111

[1] The conversion from kinematic viscosity to Saybolt universal viscosity here and in the rest of this paper was made with the aid of the conversion data of McCluer and Fenske [11].

TABLE 5.—*Adsorption, with silica gel, of a water-white distillation fraction*

[100 ml oil, plus 150 ml petroleum ether, passed through a column containing 150 g silica gel at room temperature]

Fraction	Weight	Refractive index n_D^{25}	Kinematic viscosity at—		Saybolt universal viscosity		Viscosity index
			100° F	210° F	100° F	210° F	
	g		*Stoke*	*Stoke*	sec	sec	
Original	----------	1.4734	0.3917	0.0577	182.5	44.3	95
First	15.65	1.4702	.3565	.0564	166.3	43.9	107
Second	11.60	1.4717	.3823	.0569	178.1	44.1	98
Third	13.44	1.4718	.3868	.0571	180.2	44.1	96
Fourth	13.73	1.4718	.3862	.0572	180.0	44.2	97
Fifth	10.47	1.4720	.3871	.0573	180.4	44.2	97
Silica gel hold up	13.29	1.4819	.4732	.0622	219.2	45.7	84

IX. VISCOSITY DETERMINATIONS

A knowledge of the viscosity of oil fractions and of their change in viscosity with temperature is essential in any investigation of the hydrocarbon constitution of lubricating oil. Mention has already been made of their use in connection with the systematic distillation in which blending of the oil fractions for successive distillations was done on the basis of viscosity. The temperature coefficient of viscosity is equally important, since with its aid the course of fractionation with respect to type (as accomplished by extraction with a solvent or by selective adsorption) can be followed. Consequently, the determination of viscosity after every fractionating process is an established procedure in this laboratory. Viscosities are usually determined at 100 and 210° F. Where the nature of the material makes this impossible (as with the waxes and original cuts), determinations were made with 150° F as the lower temperature.

The essentials embodied in the design of the viscosity apparatus are that (a) the viscosity should be obtainable in fundamental units of kinematic viscosity with an accuracy of about ± 1 percent and a precision of about ± 0.2 percent; (b) the sample should not exceed 10 ml and should be readily recoverable; (c) the determination of viscosity should be a routine matter with about 40 determinations per day; and (d) it should be possible to determine the density in the same apparatus.

The above conditions were fulfilled by the assembly of a series of pipettes with capillaries of different dimensions mounted vertically in oil baths thermostatically controlled to ±0.05° F. One of these pipettes mounted in the large Pyrex jar which served as a bath is shown schematically in figure 10. The bulb D and capillary F are entirely within the oil bath. The lower portion of the pipette extended through the bottom of the bath [10] into an insulated double-walled air bath regulated to ±2° F. Viscosity determinations were made by drawing the sample of oil into the pipette, allowing it to come to the temperature of the bath, and noting the time of efflux from C to E. The effluent oil was collected in its original container. The pipettes were washed in situ with benzene or toluene and dried with a current of air.

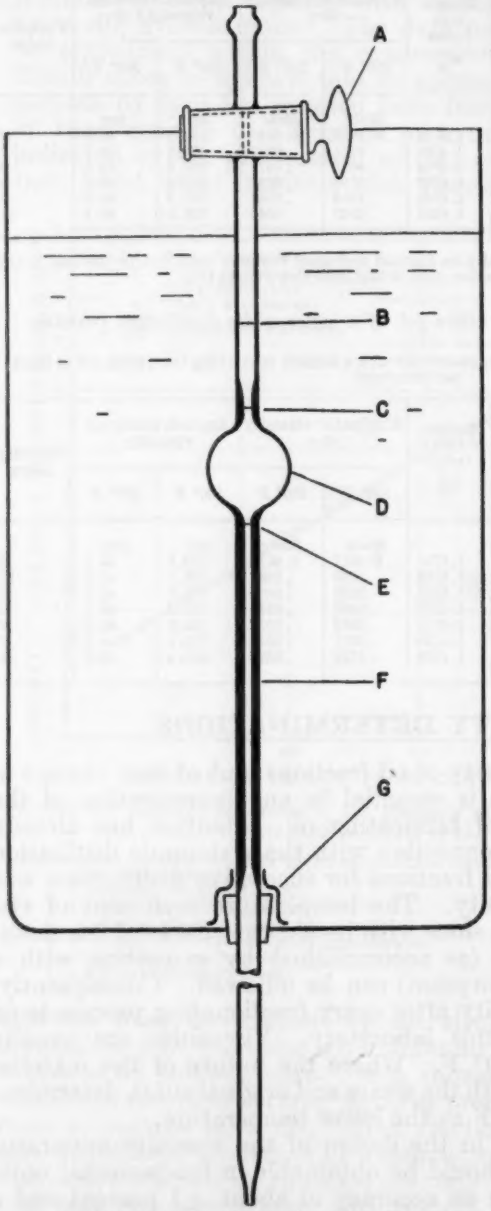

FIGURE 10.—*Viscosity pipette.*

Standard samples of oil, whose viscosities were considered accurate to ±0.5 percent, were obtained from the Heat Division of this Bureau and used to calibrate the pipettes. Each pipette was calibrated with several of these standard samples, whose viscosities covered the range for which the pipette was designed. In table 6 are given the calibration data for one pipette. The values for the viscometer constant agreed within ±0.5 percent.

[10] This was accomplished in the case of the bath operating at 210° F by ground-glass joints, and in the case of the bath operating at the lower temperature, 100° F, by rubber stoppers fitted with glass protectors (G, fig. 10) and painted with the condensation product of polyvinyl alcohol and butyraldehyde, a resin developed by T. P. Sager, of this Bureau, which gives a flexible film highly resistant to oil.

TABLE 6.—*Calibration of pipette no. 2 used in 100° F measurements*

Sample	Temperature [1]	Time of efflux	Kinematic viscosity, KV	Viscometer constant, $C=\frac{KV}{t}$
	°C	sec	*Stoke*	
SVS 1A	25.0	64.5	0.2878	4.462×10^{-3}
SVS 3A	21.9	171.5	.7697	4.489
SVS 4	21.9	382.7	1.715	4.481
SVS 6G	21.9	1,961.3	8.731	4.452
Average				4.471×10^{-3}

[1] Tests at the operating temperature of the bath, 100° F, gave the same viscometer constant (within the limits of accuracy) for a given pipette.

Densities and viscosities could be determined with one filling of the pipette. In the density determinations, oil from a weighed erlenmeyer flask was drawn up to mark B; the flask was weighed again; and the weight of oil in the pipette obtained by difference. The volume of the pipette was determined by calibration in a similar manner with oil of known density. With care a precision of about ±0.2 percent is obtainable with this method. However, the precision obtained in the routine determination of density was in some cases not better than ±1 percent.

X. CONCLUSION

From what has been accomplished so far it appears likely that the oil may be separated by distillation into substantially constant-boiling fractions, and that these fractions may be separated into hydrocarbons of different types by one of the other physical methods.

The authors desire to express their gratitude for the advice of M. R. Fenske, of Pennsylvania State College, during this investigation.

XI. LITERATURE REFERENCES

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WASHINGTON, October 8, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP850

Part of Journal of Research of the National Bureau of Standards, Volume 15, December 1935

EFFECT OF HUMIDITY IN HOT-WIRE ANEMOMETRY

By Galen B. Schubauer

ABSTRACT

The possibility of a humidity effect on the heat loss from a heated wire in an air stream has long been recognized, but only recently was the effect found experimentally by Paeschke. The effect is to increase the heat loss at the higher humidities. The present paper describes an experiment conducted to verify the existence of the effect. The results show an increase of heat loss per degree rise in wire temperature of about 2 percent for a change in the partial pressure of water vapor from 0.007 to 0.023, or a change in relative humidity from 25 to 70 percent in the neighborhood of 25° C. The effect may be explained by an effect of humidity on the thermal conductivity of air.

A hot-wire anemometer consists essentially of a small electrically heated wire, usually of platinum, which may be exposed to an air stream in which the speed is to be measured. Associated apparatus is required for controlling the heating current and measuring the rate of heat loss from the wire. The theoretical relation between the rate of heat loss and the air speed is given by the following formula due to King: [1]

$$\frac{H}{\Delta T}=4.18\, l\, (k+2\sqrt{\pi k\rho c r V}), \qquad (1)$$

where

H=heat loss from the wire to the surrounding air in watts.
ΔT=temperature elevation of the wire above the temperature of the surrounding air in degrees C.
l=length of the wire in centimeters.
k=thermal conductivity of air in cgs units.
ρ=density of air in cgs units.
c=specific heat of air at constant volume in cgs units.
r=radius of wire in centimeters.
V=air speed in centimeters per sec.

Since the heat lost from the wire by radiation is neglected in equation 1 and also since k, near the wire, and r may not be known with sufficient accuracy, the hot-wire anemometer cannot be used as an absolute instrument, but must be calibrated by measuring $H/\Delta T$, or some related quantity, in a stream of known speed. It is the universal experience of those working with hot-wire anemometers that the calibration cannot be relied upon over long periods of time. Aside from such changes as may occur due to damaging of the wire in handling, other changes of a seemingly erratic nature take place which are difficult to account for, and which have done much to discourage the use of hot-wire anemometers in precise work.

[1] L. V. King, *On the convection of heat from small cylinders in a stream of fluid: Determination of the convection constants for small platinum wires with application to hot-wire anemometry.* Phil. Trans. Roy. Soc. **214**, 373, (1914).

It has long been suspected that changes in the heat loss from the wire may occur through the effect of humidity on such quantities as k, ρ, and c in equation 1. It is known that the presence of water vapor in the air increases the thermal conductivity for small partial pressures of the vapor,[2] and for this reason an increase of heat loss with increasing humidity is to be expected. The effect of humidity on the product of density and specific heat is exceedingly small and as a contributing factor can probably be neglected. While it is possible to predict the direction of the effect from equation 1, it is difficult to estimate its magnitude due to the neglected radiation loss. Furthermore the value of k for air containing small amounts of water vapor is not definitely known at temperatures below 80° C.

An increase in the heat loss from a wire as the result of increasing the humidity was recently found experimentally by W. Paeschke.[3] An earlier attempt to find an effect of humidity, made by Kennelly and Sanborn[4] in connection with the effect of air density on the heat loss from a wire, led to the conclusion that the effect, if present, was too small to be detected. However, in the latter tests, no humidity measurements were made.

The effect was investigated at the National Bureau of Standards in a small return-circuit wind tunnel in which the relative humidity could be varied between 25 and 70 percent. The wire, which was of platinum 0.05 mm in diameter and 27.0 mm long, was placed in the working section about 10 cm from a standard pitot-static tube by which the speed was measured. The direction of the air flow was upward and normal to the wire. All accompanying apparatus, such as current controls and potentiometer, were located outside the tunnel where the humidity remained essentially constant.

The relative humidity in the tunnel could be raised from about 25 to near 70 percent in 2 or 3 hours by placing water in troughs along the tunnel walls and allowing a large area of cloth, inside the tunnel on the return-duct walls, to become wet by capillary attraction. The removal of the water and the circulation of outside air through the tunnel lowered the relative humidity to within a few percent of the outside value in about 4 hours. It was possible therefore to change rather quickly from one condition to another without the necessity of changing the temperature or disturbing the experimental setup. The relative humidity was measured by a hair hygrometer, which had previously been calibrated.

Since the air temperature changed but little, varying only between 23 and 27° C, and the barometric pressure remained essentially constant at 756 mm of mercury, the humidity changes were really changes in the absolute humidity. By taking into account the temperature changes, the readings of the hygrometer were converted into absolute numidities. These are expressed here in terms of the partial pressure of water vapor, denoted by p_2.

The experimental procedure consisted in measuring the potential drop across the wire at various wind speeds for a constant heating current. The wire temperature was allowed to vary with the speed. Using these data together with the temperature resistance curve for

[2] H. A. Daynes, Gas Analysis by Measurement of Thermal Conductivity. Cambridge University Press, p. 23 (1933).
[3] W. Paeschke, *Feuchtigkeitseffekt bei Hitzdrahtmessungen*, Physik Z. 36, 564 (1935).
[4] A. E. Kennelly and H. S. Sanborn, *The influence of atmospheric pressure upon the forced thermal convection from small electrically heated platinum wires*, Proc. Am. Phil. Soc. 52, 55 (1914).

the wire, which was obtained by measurements of the wire resistance at the temperature of the surrounding air, $H/\Delta T$, the heat loss per degree rise in temperature, was calculated. From a number of such determina-

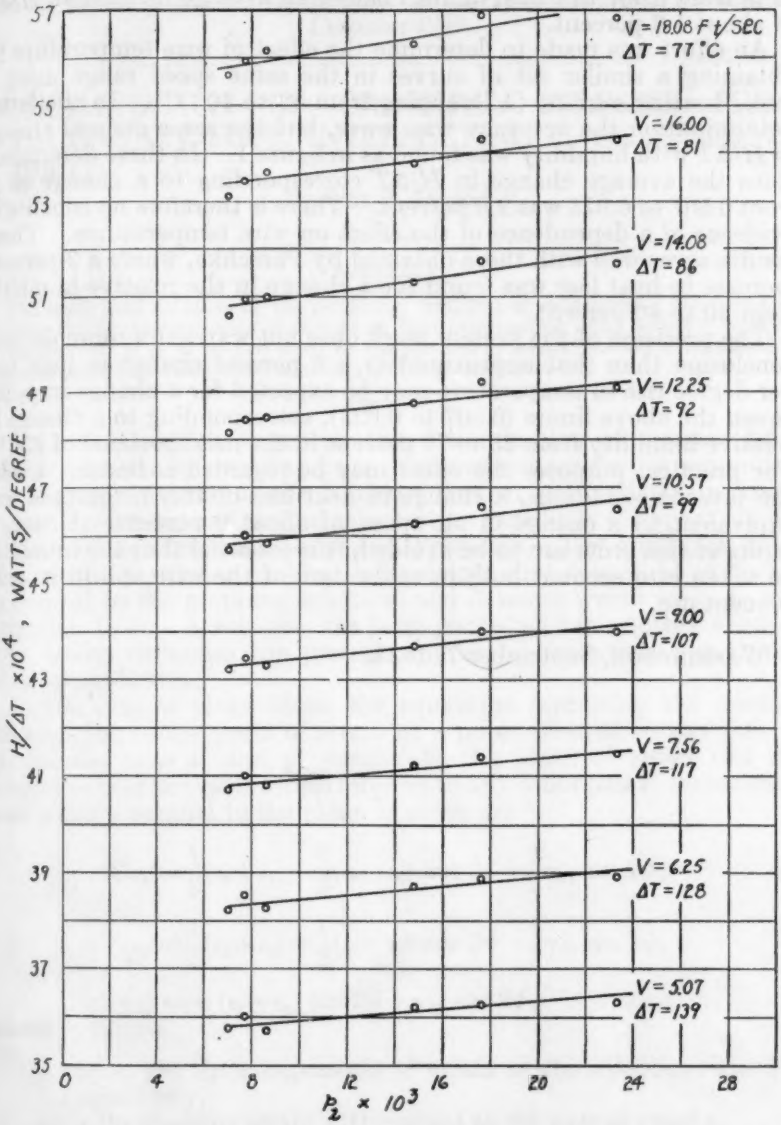

FIGURE 1.—*Variation of heat loss per degree rise in wire temperature with variation in humidity.*

(p_2=partial pressure of water vapor.)

tions corresponding to several relative humidities ranging from 25 to 70 percent, the variation in $H/\Delta T$ with humidity was determined.

The results obtained with a heating current of 0.464 ampere are summarized in figure 1. The spacing between curves in this figure

is determined by the change in $H/\Delta T$ in going from one speed to the next. The approximate temperature elevation ΔT of the wire corresponding to the various speeds is also shown. Considering a change in p_2 from 0.007 to 0.023, figure 1 shows an average increase in $H/\Delta T$ of about 1.8 percent.

An effort was made to determine the effect of wire temperature by obtaining a similar set of curves in the same speed range using a lower heating current (ΔT ranging from 42 to 70° C). In the latter determination the accuracy was lower, but the same general change in $H/\Delta T$ with humidity was found as in figure 1. In these determinations the average change in $H/\Delta T$ corresponding to a change in p_2 from 0.007 to 0.023 was 2.0 percent. There is therefore no conclusive evidence of a dependence of the effect on wire temperatures. These results agree well with those obtained by Paeschke, where a 2-percent increase in heat loss was found for a change in the relative humidity from 30 to 80 percent.

The precision of the present work does not warrant a more definite conclusion than that approximately a 2 percent change in heat loss per degree rise in temperature may be expected for a change in p_2 between the above limits (0.007 to 0.023), corresponding to a change in relative humidity from 25 to 70 percent in the neighborhood of 25° C. For practical purposes the effect may be regarded as linear. Under the present conditions, a change in heat loss of this magnitude was equivalent to a change in air speed of about 6 percent. Hence, if errors of this order are to be avoided, it is essential that the humidity be taken into account both in calibration of the wire and in its subsequent use.

WASHINGTON, September 7, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP851

Part of Journal of Research of the National Bureau of Standards, Volume 15, December 1935

DETERMINATION OF PRINCIPAL STRESSES FROM STRAINS ON FOUR INTERSECTING GAGE LINES 45° APART

By Wm. R. Osgood

ABSTRACT

The analytical solution of the particular problem of determining the principal stresses from measurements of strains on four intersecting gage lines 45° apart is so simple that it is to be preferred to the general graphical solution published in a previous paper. The analytical solution is given here.

Since the original paper on the determination of stresses from strains on three intersecting gage lines was written,[1] an investigation has been undertaken at the National Bureau of Standards in which strains were measured on four intersecting gage lines 45° apart for the purpose of determining the principal stresses. The analytical solution of this particular problem is so simple that it is to be preferred in general to the graphical solution, and it seems worth while to call attention to it. A solution has been published [2] in another connection, which embodies the present one in all essentials but is not directly applicable.

In the case of plane stress the equations expressing the relation between the components of strain at a point referred to any pair of rectangular axes x' and y' parallel to the plane of stress and the components of the same strain referred to any other pair of rectangular axes x and y parallel to the plane of stress are [3]

$$\epsilon_{x'}=\frac{1}{2}(\epsilon_x+\epsilon_y)+\frac{1}{2}(\epsilon_x-\epsilon_y)\cos 2\psi+\frac{1}{2}\gamma_{xy}\sin 2\psi, \tag{1}$$

$$\epsilon_{y'}=\frac{1}{2}(\epsilon_x+\epsilon_y)-\frac{1}{2}(\epsilon_x-\epsilon_y)\cos 2\psi-\frac{1}{2}\gamma_{xy}\sin 2\psi, \tag{2}$$

$$\gamma_{x'y'}=-(\epsilon_x-\epsilon_y)\sin 2\psi+\gamma_{xy}\cos 2\psi, \tag{3}$$

where

ϵ_x and ϵ_y are the components of strain in the directions x and y, respectively,

γ_{xy} is the shearing strain with respect to the axes of x and y,

ψ is the angle measured positive counterclockwise from the positive axis of x to the positive axis of x',

$\epsilon_{x'}$ and $\epsilon_{y'}$ are the components of strain in the directions x' and y', respectively, and

$\gamma_{x'y'}$ is the shearing strain with respect to the axes of x' and y'.

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Suppose that strains have been measured (tensile strain as positive) along four intersecting gage lines, 1 and 3, 90° apart, and 2 and 4, 90° apart and making angles of 45°, respectively, with 1 and 3. Then the maximum and minimum principal strains, ϵ_u and ϵ_v, respectively, in the plane of stress and the directions of these strains may be

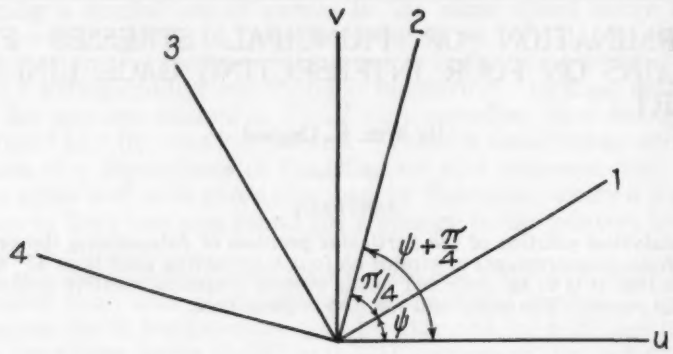

FIGURE 1.—*Four intersecting gage lines (1, 2, 3, 4) and directions (u, v) of principal strains.*

obtained as follows. If we take the directions of x' and y' in the directions of the maximum and minimum principal strains, ϵ_u and ϵ_v, respectively, we obtain from equations 1 and 2

$$\epsilon_1=\frac{1}{2}(\epsilon_u+\epsilon_v)+\frac{1}{2}(\epsilon_u-\epsilon_v)\cos 2\psi, \tag{4}$$

$$\epsilon_2=\frac{1}{2}(\epsilon_u+\epsilon_v)-\frac{1}{2}(\epsilon_u-\epsilon_v)\sin 2\psi, \tag{5}$$

$$\epsilon_3=\frac{1}{2}(\epsilon_u+\epsilon_v)-\frac{1}{2}(\epsilon_u-\epsilon_v)\cos 2\psi, \tag{6}$$

$$\epsilon_4=\frac{1}{2}(\epsilon_u+\epsilon_v)+\frac{1}{2}(\epsilon_u-\epsilon_v)\sin 2\psi. \tag{7}$$

The four simultaneous equations 4, 5, 6, and 7 contain only three unknowns, ϵ_u, ϵ_v, and ψ. The best solution can be shown by the method of least squares to be

$$\epsilon_u=\frac{1}{2}\left[\frac{1}{2}(\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4)+\sqrt{(\epsilon_1-\epsilon_3)^2+(\epsilon_2-\epsilon_4)^2}\right], \tag{8}$$

$$\epsilon_v=\frac{1}{2}\left[\frac{1}{2}(\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4)-\sqrt{(\epsilon_1-\epsilon_3)^2+(\epsilon_2-\epsilon_4)^2}\right], \tag{9}$$

$$\tan 2\psi=-\frac{\epsilon_2-\epsilon_4}{\epsilon_1-\epsilon_3}. \tag{10}$$

The maximum and minimum principal stresses, σ_u and σ_v, respectively, in the plane of stress are then obtained as

$$\sigma_u=\frac{E}{1-m^2}(\epsilon_u+m\epsilon_v), \tag{11}$$

$$\sigma_v=\frac{E}{1-m^2}(\epsilon_v+m\epsilon_u), \tag{12}$$

where E is the modulus of elasticity, and m is Poisson's ratio. By substituting the values of ϵ_u and ϵ_v from equations 8 and 9 in equations 11 and 12, the principal stresses σ_u and σ_v may be expressed directly in terms of the observed components of strain ϵ_1, ϵ_2, ϵ_3, and ϵ_4:

$$\sigma_u=\frac{E}{2(1+m)}\left[\frac{1}{2}\frac{1+m}{1-m}(\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4)+\sqrt{(\epsilon_1-\epsilon_3)^2+(\epsilon_2-\epsilon_4)^2}\right], \tag{13}$$

$$\sigma_v=\frac{E}{2(1+m)}\left[\frac{1}{2}\frac{1+m}{1-m}(\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4)-\sqrt{(\epsilon_1-\epsilon_3)^2+(\epsilon_2-\epsilon_4)^2}\right]. \tag{14}$$

For most purposes it is probably adequate to assume $m=\frac{1}{3}$, in which case the expressions for the principal stresses reduce to the simpler form

$$\sigma_u=\frac{3E}{8}\left[\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4+\sqrt{(\epsilon_1-\epsilon_3)^2+(\epsilon_2-\epsilon_4)^2}\right], \tag{15}$$

$$\sigma_v=\frac{3E}{8}\left[\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4-\sqrt{(\epsilon_1-\epsilon_3)^2+(\epsilon_2-\epsilon_4)^2}\right]. \tag{16}$$

WASHINGTON, September 30, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP852

Part of Journal of Research of the National Bureau of Standards, Volume 15, December 1935

STABILITY OF AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

By James I. Hoffman

ABSTRACT

The tests described show that aqueous solutions of acid potassium phthalate stored in tightly stoppered flasks do not decompose under the conditions existing in the average chemical laboratory.

Occasional inquiries at this Bureau indicate that some chemists prefer to take aliquot portions of a master solution of acid potassium phthalate for the standardization of alkaline solutions rather than to weigh separate portions of the reagent for each titration. There has been considerable doubt concerning the "keeping" qualities of a solution of acid potassium phthalate. The following tests were therefore made.

A solution was prepared by dissolving 10.0000 g of acid potassium phthalate (National Bureau of Standards Standard Sample 84) in distilled water and diluting to 1 liter in a volumetric flask made of soft glass. After thorough mixing, about one-half of this solution was transferred to a dry Pyrex flask. Both flasks were closed with tightly fitting glass stoppers which were sealed with Cementyte. The regular supply of distilled water was used, and no attempt was made to sterilize it. After allowing the solutions to stand for 1 year in a cupboard in a north laboratory, 100.00-ml portions (equivalent to 1.0000 g of phthalate) were withdrawn and titrated with an approximately 0.15 *N* solution of sodium hydroxide. At the same time 1.0000-g portions of acid potassium phthalate from the same lot were dissolved in 100 ml of distilled water and immediately titrated with the 0.15 *N* sodium hydroxide solution. All the results agreed within 1 part in 3,000.

The flasks were again tightly sealed, and the solutions remaining in the flasks were then exposed outdoors to direct sunlight, 2 to 5 hours at a time, during June, July, and August. The total time of exposure to direct sunlight was 75 hours, but the elapsed time was 3 months. Comparative titrations again showed an agreement within 1 part in 3,000 between 100.00-ml portions of these solutions and solutions freshly prepared by dissolving 1.0000 g of phthalate in 100 ml of distilled water.

Volumetric glassware was specially calibrated for this work, and the temperature of the solutions at the time of preparation and withdrawal of the aliquot portions was the same (27° C). Weight burettes were used in all titrations. The solutions remained clear, and there was no evidence of fungous growth.

The tests show that, under the conditions existing in the average laboratory, standard aqueous solutions of acid potassium phthalate do not change in strength and can be used in acidimetry if desired. However, the use of such solutions has not been adopted at this Bureau because the present procedure of weighing the phthalate, dissolving it in water, and immediately titrating the solution with alkali is so extremely simple.

WASHINGTON, October 2, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP853

Part of Journal of Research of the National Bureau of Standards, Volume 15, December 1935

DETERMINATION OF GALLIUM IN ALUMINUM

By J. A. Scherrer

ABSTRACT

Two procedures are described for the gravimetric determination of gallium in aluminum. One of these is based upon the separation of gallium from aluminum in sulphuric-acid solution by precipitation with cupferron. In this method, gallium is determined by difference in an oxide residue containing gallium, vanadium, titanium, and zirconium. The other procedure is based upon the separation of gallium from aluminum in hydrochloric-acid solution by extraction with ether. In this method, gallium is determined directly as the oxide Ga_2O_3.

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I. INTRODUCTION

In the preparation of a pure metal on a commercial scale, it is impossible to eliminate completely all impurities. The metal will be found to be slightly contaminated by those elements which are present in the ore and have somewhat similar properties, and by those which are unavoidably introduced from the reagents and the apparatus used.

Gallium is an element of the first type, for it is widely distributed in bauxites and accompanies aluminum to some extent in its reduction to metal. Methods for its determination are therefore of importance, not only to ascertain how much of it is present, but also to be able to correct for its effect in determinations of other constituents by methods that are subject to the interference of gallium.

Gallium is quantitatively precipitated by cupferron (ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N.NO.ONH_4$) in sulphuric-acid solution. By this means it can be separated from aluminum. Gallium can also be separated from aluminum in hydrochloric-acid solution, by extraction with ether. If gallium only is being determined, the method of extraction with ether is preferable, because the final precipitate obtained is gallic oxide, Ga_2O_3. If, however, such

elements as iron, vanadium, titanium, and zirconium are also being determined, the method in which the gallium is separated from aluminum by precipitation with cupferron is preferable. It should be observed that in the latter method gallium is determined by difference, and therefore the accuracy is less than can be attained by the method of extraction with ether.

II. METHODS RECOMMENDED FOR THE DETERMINATION OF GALLIUM IN ALUMINUM

1. PROCEDURE BASED UPON THE JOINT SEPARATION OF GALLIUM, VANADIUM, TITANIUM, ZIRCONIUM, IRON, TIN, AND COPPER BY PRECIPITATION WITH CUPFERRON

Place 10 g of the sample in a 600-ml beaker, add 200 ml of water, cover the beaker, and then add cautiously 200 ml of hydrochloric acid.[1] When the sample has dissolved, carefully add 60 ml of sulphuric acid (an excess of 30 ml over that which is necessary to combine with the aluminum), and evaporate the resulting solution until hydrochloric acid is expelled and vapors of sulphuric acid are evolved. Dilute the solution to 300 ml and filter it in order to remove any silica. Ignite the siliceous residue, treat it with about 10 ml of hydrofluoric acid (48 percent) and 1 ml of sulphuric acid, heat the resulting solution until vapors of sulphuric acid are evolved, dilute it, and finally add it to the filtrate obtained above. Dilute the solution to 375 ml, chill it in ice water, and add to it about 20 ml of a chilled, filtered, freshly prepared, 6-percent solution of cupferron. Allow the solution with the precipitate to stand in ice water for 1 hour, and stir it occasionally. In order to facilitate filtration, add a small amount of paper pulp.

Filter the solution and wash the precipitate with chilled diluted sulphuric acid (7+93) containing about 1.5 g of cupferron per liter. Place the filter and precipitate in a platinum crucible and ignite them at as low a temperature as possible, preferably by placing the crucible in a cold muffle furnace and gradually increasing the temperature to about 550° C. Dissolve the ignited residue in diluted hydrochloric acid (9+1), transfer the resulting solution to a 250-ml beaker, and add to it 5 ml of sulphuric acid. Evaporate the solution until vapors of sulphuric acid are evolved.

Since the precipitate obtained with cupferron consists not only of gallium but of a number of other elements as well, it is necessary to eliminate or to determine these other elements in order to evaluate the gallium.

(a) REMOVAL OF TIN AND COPPER

Dilute the sulphuric-acid solution to 100 ml, add 5 g of tartaric acid, and stir until the crystals are dissolved. Digest the solution on the steam bath until the iron is completely dissolved, and then dilute it to 250 ml. Pass a stream of hydrogen sulphide through the solution at room temperature for 15 to 20 minutes, and then let it stand for one-half hour before filtering it. Wash the filter and precipitate two or three times with diluted hydrochloric acid (1+200) which has been saturated with hydrogen sulphide. The

[1] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; sulphuric acid, the concentrated acid of specific gravity 1.84; and nitric acid, the concentrated acid of specific gravity 1.42. Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean 1 volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.

precipitation and filtration are made in order to remove copper and tin, as well as any other metal which precipitates with hydrogen sulphide in acid solution.

(b) REMOVAL OF IRON

Nearly neutralize with ammonium hydroxide the filtrate obtained above, and pass in hydrogen sulphide for about 5 minutes to insure the reduction of iron to the bivalent state. Add an excess of 10 ml of ammonium hydroxide, and saturate the solution with hydrogen sulphide. Filter the solution, and wash the precipitate four times with a 2-percent solution of ammonium sulphide which also contains 1 percent of ammonium tartrate.

(c) RECOVERY OF GALLIUM, VANADIUM, TITANIUM, AND ZIRCONIUM BY CUPFERRON

After the removal of those metals which are precipitated by hydrogen sulphide in acid solution, and of iron, it is necessary to recover the gallium from solution. This is most conveniently done by again precipitating it with cupferron. It should be observed that the precipitate will be contaminated by those elements which also form insoluble compounds with cupferron under the same conditions.

Acidify with sulphuric acid the filtrate obtained in the removal of iron and boil it until the hydrogen sulphide is expelled. Filter the solution, dilute it to 375 ml, neutralize it with ammonium hydroxide, and finally add to it 30 ml of sulphuric acid. Chill the resulting solution in ice water, add to it 15 to 20 ml of the chilled 6-percent solution of cupferron, stir it well, and allow it to stand for about 1 hour. Filter the solution, and wash the precipitate with chilled diluted sulphuric acid (7+93) containing about 1.5 g of cupferron per liter. Place the filter and precipitate in a platinum crucible, dry them carefully, char them, and finally ignite them for a few minutes at 1,000° C. Weigh the residue as a mixture of Ga_2O_3, V_2O_5, TiO_2, and ZrO_2.

(d) DETERMINATION OF VANADIUM

Fuse the mixture of oxides obtained above with 0.5 g of potassium pyrosulphate. Dissolve the fused mass in 10 ml of diluted sulphuric acid (1+9), and add to the resulting solution 5 ml of a solution of ferric sulphate (equivalent to 25 mg of iron) and 12 ml of a 25-percent solution of sodium hydroxide. The solution at this stage should have a volume of about 30 ml and should contain an excess of about 1.5 g of sodium hydroxide. Boil the solution for 1 to 3 minutes, filter it, and wash the precipitate twice with a 1-percent solution of sodium hydroxide. Because the amount of vanadium involved is so small, it is rarely necessary to repeat the precipitation. Neutralize the filtrate with diluted sulphuric acid (1+4), then add 5 ml of sulphuric acid, and concentrate by evaporation to a volume of about 25 ml. Cool the solution to room temperature, transfer it to a comparison cylinder, and add 3 ml of a 3-percent solution (by volume) of hydrogen peroxide. The volume should not be over 30 ml at this stage. Determine the vanadium colorimetrically by comparing the solution with one of known vanadium content which has been similarly treated.

(e) DETERMINATION OF TITANIUM

Dissolve the precipitate obtained with sodium hydroxide by pouring 20 ml of hot diluted sulphuric acid (1+9) repeatedly through the filter, and then wash the filter with sulphuric acid of the same strength.

If necessary, concentrate the solution by evaporation until its volume is not greater than 20 ml. Cool the solution to room temperature, transfer it to a comparison cylinder, and add 3 ml of a 3-percent solution of hydrogen peroxide. Determine the titanium colorimetrically by comparing the solution with one of known titanium content which has been similarly treated.

(f) DETERMINATION OF ZIRCONIUM

After the colorimetric determination of titanium, transfer the solution to a small beaker, add to it an excess of diammonium phosphate (10 to 50 mg usually suffices), and allow it to stand at 50° C for several hours, or until the zirconium phosphate is coagulated. It should be noted that a sufficient amount of hydrogen peroxide should be in the solution during this treatment to keep the titanium in the peroxidized condition. Filter the solution and wash the phosphate precipitate with a 5-percent solution of ammonium nitrate. Transfer the filter and the precipitate to a platinum crucible, ignite carefully until the paper is destroyed, and then heat for a few minutes at 1,000° C. Weigh the residue as $ZrO(PO_3)_2$.

(g) DETERMINATION OF GALLIUM BY DIFFERENCE

In order to arrive at a determination of gallium, it is necessary to subtract from the weight of the mixed oxides of gallium, vanadium, titanium, and zirconium, obtained from the second precipitation by cupferron, the weights of V_2O_5, TiO_2, and ZrO_2 determined as has just been described. It is to be noted that gallium is thus determined by difference.

2. PROCEDURE BASED UPON THE EXTRACTION OF GALLIUM BY ETHER

Gallium can be determined directly by proceeding in the following manner:

Place 10 g of the sample in a 600-ml beaker, add 200 ml of water, cover the beaker, and then add cautiously 250 ml of hydrochloric acid. When the sample has dissolved, evaporate the solution to about 300 ml, cool it, and dilute it to 400 ml with diluted hydrochloric acid (1+1). Transfer the solution to a separatory funnel, and cool in ice water. Add to the cooled solution 150 ml of ether which has also been cooled. If both the ether and the acid solution are cold when mixed, the formation of a yellow color, which usually appears, can be to a great extent prevented. Shake the contents of the separatory funnel thoroughly, and then chill again by immersion in ice water. When the layers have separated, draw off the acid solution and transfer the ether extract to a beaker. In this treatment the gallium as chloride passes into the ether while the aluminum remains in the acid solution. Make two more ether extractions, using 50 ml of ether in each extraction. In the third extraction, allow the separatory funnel to stand at room temperature for about 1 hour before removing the acid solution.

Combine the three ether extracts and let stand at room temperature or in a warm place until the ether layer becomes entirely separated from the small amount of acid solution which had been unavoidably entrained. Carefully remove this small amount of acid solution and treat it with two small portions of ether. Transfer the entire ether fraction, which now contains all the gallium, to a clean beaker and

evaporate it carefully to dryness. Dissolve the residue obtained in nitric acid, add 5 ml of sulphuric acid, and heat until vapors of sulphuric acid are evolved. Insure the destruction of organic matter by adding small portions of nitric acid from time to time, and continue to heat until vapors of sulphuric acid appear.

Remove the metals which are precipitable by hydrogen sulphide in acid solution, and also iron, as previously directed. Recover the gallium by precipitation with cupferron as previously directed. Weigh the ignited residue as Ga_2O_3.

The results obtained in the recovery of known quantities of gallium, which had been added to solutions containing 10-g portions of aluminum (Standard Sample 44c), by the method of extraction with ether are given in table 1.

TABLE 1.—*Recovery of gallium from solutions of aluminum to which known quantities of gallium were added*

Gallium present [1]	Gallium recovered	Error
g	g	g
0.0006	0.0006	0.0000
.0007	.0009	+.0002
.0011	.0013	+.0002
.0100	.0099	−.0001
.0102	.0101	−.0001

[1] This includes the gallium added as well as that contained in the aluminum.

The results obtained in the determination of gallium in four different samples of aluminum by the two procedures described are given in table 2.

TABLE 2.—*Comparison of the results obtained in the determination of gallium in aluminum by the two procedures*

Cupferron method	Ether method	NBS sample number of aluminum used
Percent	*Percent*	
0.017	0.016	44
.017	.017	
	.018	
.020	.020	44a
.020	.021	
.020	.024	
.022		
.011	.010	44b
.012	.010	
.013	.011	
.013		
.0003	.0004	44c
.0004	.0007	

In the case of Standard Sample 44c, gallium was determined in the combined cupferron precipitates, as well as in the combined ether extracts, of five 10-g portions of aluminum. The final residues of Ga_2O_3 were examined spectrochemically by Bourdon F. Scribner, of this Bureau, who identified gallium, and found in them only minute amounts of impurities originally in the aluminum.

III. DISCUSSION OF THE METHODS

Although it has been generally believed that gallium is not completely precipitated by cupferron in solutions containing as much as 5 percent of sulphuric acid by volume, when tartaric acid is present, and that complete precipitation is not attained in solutions having an acidity greater than 6 ml of sulphuric acid in 400 ml,[2] it was found that no difficulty was encountered in producing complete precipitation in solutions containing as much as 7 to 8 percent of sulphuric acid by volume, provided that an excess of cupferron (15 to 20 ml of a 6-percent solution) was added. It was found necessary with this method to work with volumes of 400 ml, in order to prevent precipitation of aluminum salts by crystallization when the solutions were chilled.

In the determination of gallium in aluminum, if the gallium content is as much as 0.01 percent, a 10-g portion is sufficient. If the content is smaller, the cupferron precipitates resulting from a number of 10-g portions should be combined to yield at least 0.001 g of ignited mixed oxides. In the mixed oxide residue, 0.1 mg of either titanium or vanadium can be easily determined colorimetrically if the volumes of the solutions are kept small. The determination of small amounts of zirconium is somewhat difficult, but 0.1 mg (0.3 mg of $ZrO(PO_3)_2$) of this element can be handled if again the volume of the solution is kept small.

It had been found by Swift [3] that 97 percent of the gallium contained in a hydrochloric-acid solution of acidity 4.9 to 5.9 *N* could be extracted by ether in one operation. In order to ascertain the number of extractions necessary to remove all the gallium, the following experiments were made. Two hydrochloric-acid solutions, each containing 10 g of aluminum and 0.0076 g of gallium, were extracted four times. There was recovered from the first extraction 0.0069 and 0.0065 g of gallium, respectively; from the second, 0.0004 and 0.0006 g; and from the third, 0.0003 and 0.0003 g. The fourth extract was found to contain less than 0.0001 g of gallium. The total amounts of metal recovered were 0.0076 and 0.0074 g, respectively. In another experiment, in which 0.0102 g of gallium was added, the recoveries from three extractions were 0.0078, 0.0016, and 0.0008 g, a total recovery of 0.0102 g. It thus appeared that three extractions were necessary and sufficient. It should be observed that in the extraction with ether a quantity of aluminum greater than 10 g cannot be handled conveniently. In this method the volume of the acid solution is kept large enough to prevent the precipitation of $AlCl_3.6H_2O$, the solubility of which decreases with increasing concentration of hydrochloric acid and which is also affected by the presence of ether. A concentration of hydrochloric acid greater than 6 *N* should not be used, because of the solubility of the ether in solutions of higher acid concentration than this.

It should be noted that no titanium, vanadium, nor zirconium was ever found in the final residue of Ga_2O_3 obtained by the method of extraction with ether. The residue always contained a minute amount of iron, probably introduced through the reagents used. Determinations of iron in three of these residues ranged from 0.02 to 0.05 mg.

WASHINGTON, September 20, 1935.

[2] E. S. von Bergkampf, Z. anal. Chem. **83**, 345 (1931); **90**, 333 (1932).
[3] E. H. Swift, J. Am. Chem. Soc. **46**, 2375 (1924).

U. S. Department of Commerce National Bureau of Standards

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ACCELERATED SERVICE TESTS OF PINTLE BEARINGS

By Ambrose H. Stang and Leroy R. Sweetman

ABSTRACT

Accelerated service tests of pintle bearings with different combinations of materials for the pintles and cups, different pressures, and different conditions of lubrication were made under conditions similar to those which might obtain in practice as to the line of thrust and angle of swing. The bearings were under water during the tests.

The results indicated that of the materials tested one must be phosphor bronze to give satisfactory service for pressures as great as 2,000 lb/in.^{2} Pintles of H-monel, M-monel, and S-monel, gave satisfactory service at this pressure with phosphor-bronze cups.

Cups of stainless steel, chromium steel, chromium-nickel steel, malleable cast iron, and monel alloys were scored badly after only a few cycles when tested under a pressure of 2,000 lb/in.^{2} Aluminum-bronze cups were worn excessively at a comparative small number of cycles. Phosphor bronze was the only cup material tested in this investigation which gave satisfactory service with a pressure as great as 2,000 lb/in.^{2}

A stainless-steel pintle and phosphor-bronze cup provided with grooves for water circulation and tested under a pressure of 4,000 lb/in.^{2} withstood more than 288,000 cycles, the number of cycles expected in 20 years' service. A stainless-steel pintle and phosphor-bronze cup lubricated with white lead or with grease having a lead-soap base and asphalt content, did not fail when tested under a pressure of 6,000 lb/in.^{2} and subjected to more than 288,000 cycles.

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I. INTRODUCTION

The contemplated use of relatively large lock gates in the Tennessee River Valley development made it seem advisable to study, with more than the usual care, the properties of the materials used in the various elements of the gates so that long, continuous, and satisfactory service might be expected. The pintle bearings, consisting of pintles and cups, are important parts of the lock gates. Because of the heavy weight of the gates, either large pintles or high bearing pressures on the pintles must be used. Few data are available as to the relative wearing qualities of different materials for pintles or cups or as to the

greatest pressures which would give satisfactory service for pintle bearings of given materials.

The War Department, United States Engineer Office, therefore requested the National Bureau of Standards to make accelerated service tests of pintle bearings with different combinations of materials, pressures, and conditions of lubrication.

II. SPECIMENS AND TESTING PROCEDURE

Pintles having a diameter of 26 inches and subjected to bearing pressures of 2,100 lb/in.^{2} are contemplated for use at the Pickwick Lock, Tennessee River. The tangent of the angle between the axis of the pintle and the line of the resultant force on the surface of the pintle is about 0.4. The gates will swing through an angle of 70°, requiring about 1 minute for opening or closing. The pintle bearings will, of course, be under water. The estimated traffic through the lock may require the operation of the gates about 40 times a day. A life of 20 years or 288,000 cycles may be considered as satisfactory service.

It was desired that the tests at the National Bureau of Standards be carried out under conditions as similar to these as practicable, with, however, a smaller pintle.

A pintle diameter of 1 inch was considered satisfactory, and the dimensions of the pintles and cups are shown in figure 1. For the purpose of calculating bearing pressures on the pintles, the area in bearing was considered as the projected area of the cup hemisphere on a plane normal to the line of thrust and was equal to the area of half a circle, plus the area of half an ellipse, as indicated in figure 1. The tangent of the angle between the pintle axis and the line of thrust was maintained at the 0.4 value and the angle of swing for each cycle was 70°. All tests were made with the pintle bearing under water. It was necessary to conduct the tests at a faster rate than that at which the gates would be operated to obtain results within a reasonable time. Consequently, the tests were made at the rate of about 120 cycles per minute.

It is recognized that, under actual service conditions, time, water temperature, and presence of silt may have important effects on the corroding and wearing qualities of pintle bearings. These factors, which were not effective in the accelerated tests, should be given consideration in the selection of materials on the basis of the results of these tests.

The tests were carried out in a screw-power beam and poise testing machine having a capacity of 50,000 lb. To secure stability as the relative motion between the pintle and cup took place, two tests were made at the same time, as shown in figures 2 and 3.

The cups remained stationary during the tests. They were restrained from turning in the blocks in which they were placed, as shown in figure 1, by setscrews. As wear occurred each cup was adjusted vertically by means of the threaded plug in the cup block (see fig. 1) so as to maintain the correct angle for the line of thrust. Horizontal measurements (H) between pins on the thrust bars and vertical measurements (V) between the upper surface of a small rod set in the base of the testing fixture and the center of the pin connect-

ing the thrust bars (see fig. 3 and 4) could be made at any time as a check on the correctness of the angle of thrust.

The pintles were held in pintle supports, as shown in figure 1, and prevented from rotating with respect to the supports by setscrews. The bottom of the pintles rested on threaded plugs in the supports

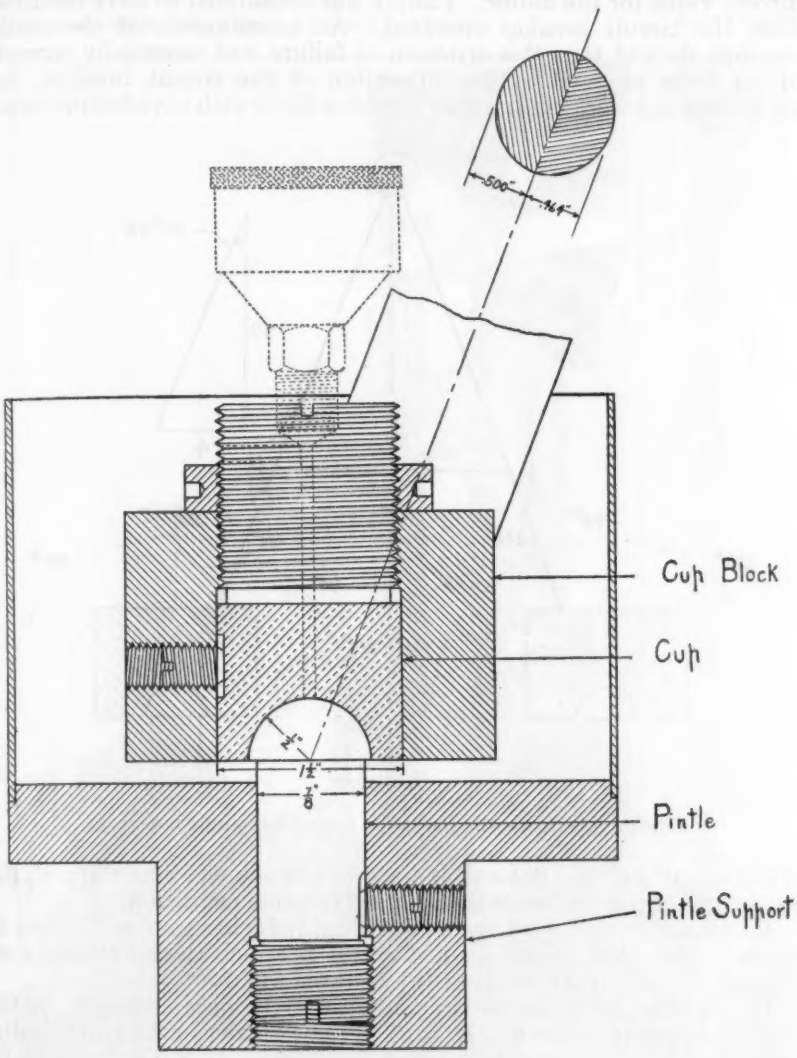

FIGURE 1.—*Testing fixtures.*

which could be adjusted vertically so that the centers of the two pintle hemispheres were at the same elevation above the tops of radial and thrust bearings, shown in figure 4. This adjustment was necessary only because of slight variations in the lengths of the pintle stems. The pintle supports, filled with water to cover the pintles, are shown in figure 5. The supports were connected by a link and were oscillated through the 70° angle by a 0.5-hp electric motor and

a reducing gear, shown in figure 2. The indication of an ammeter in the armature circuit of the motor was used as a measure of the relative power necessary to oscillate the pintle supports. A circuit breaker in the power line supplying this motor was adjusted to stop the test when the ammeter reading was about as large as the safe current value for the motor. Failure was considered to have occurred when the circuit breaker operated. An examination of the pintle bearings showed that this criterion of failure was essentially correct. In the tests stopped by the operation of the circuit breaker, the pintle bearings were in each case scored or filled with abraded material.

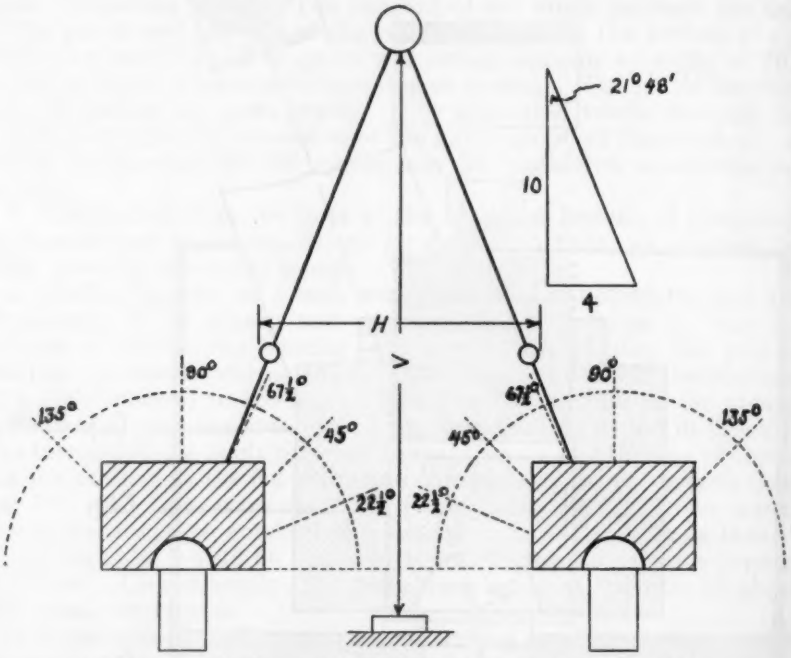

FIGURE 3.—*Schematic sketch for testing two pintle bearings.*

If the circuit breaker did not operate before the test was stopped, the pintle and cup were smooth and in serviceable condition.

A counter operated by the shaft of the reducing gear and shown in figure 2, indicated the number of cycles to which the specimens were subjected. The least count of the counter was 100 cycles.

The changes in radius of the pintle and cup were measured by the devices shown in figure 6. In each of these devices a micrometer dial gage was rigidly attached to a base plate. A V block could be rotated about a pin set in the base plate. The axis of the pin intersected the axis of the dial-gage spindle and passed through the center of the spherical surface of the pintle or cup when the specimen was set against a stop on the V block. Since the pintle or the cup could be rotated in the V block and the V block rotated about the axis through the center of the sphere, the devices could be used for radius measurements over nearly the entire hemispherical surfaces of the

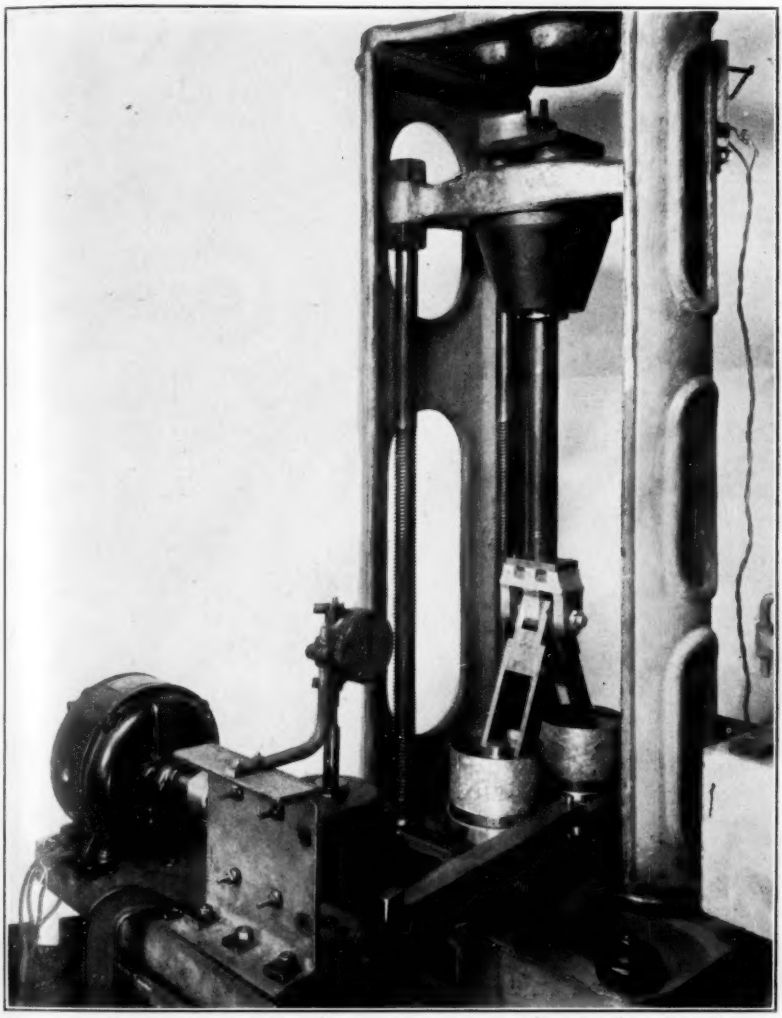

FIGURE 2.—*Apparatus assembled in the testing machine.*

FIGURE 4.—*Combination thrust and radial bearings and the cup-holding assembly.*

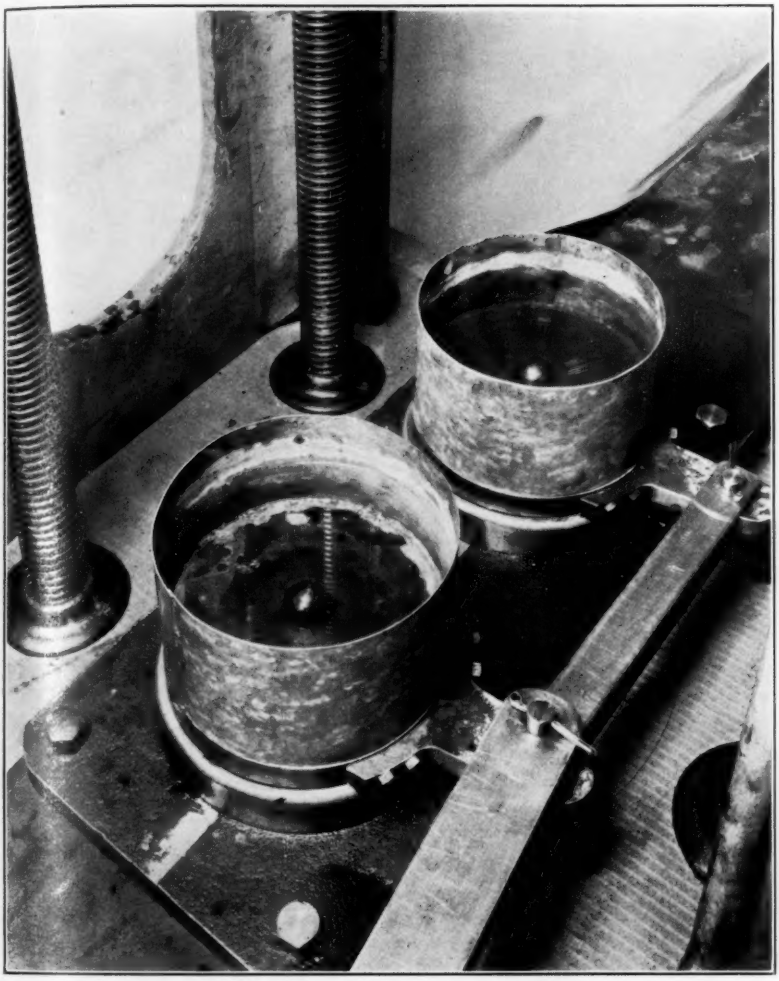

FIGURE 5.—*Pintles in the oscillating pintle supports, covered with water.*

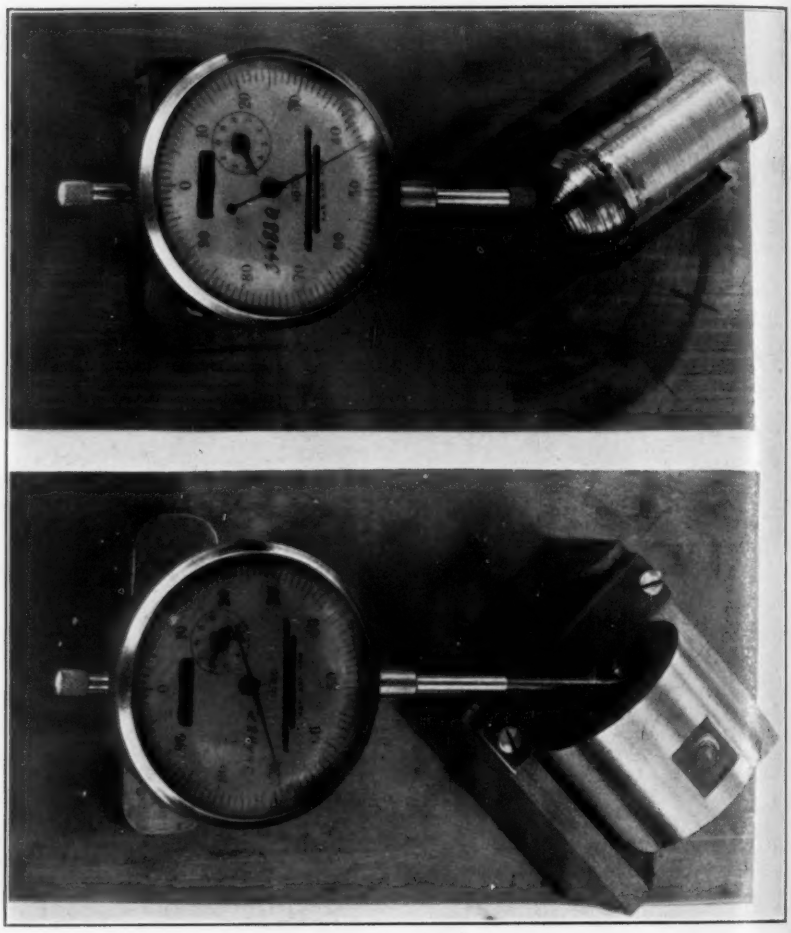

FIGURE 6.—*Devices for measuring the change in radius of the pintles and cups.*

specimens. Readings were taken, however, only in the plane determined by the lines of thrust and the line connecting the centers of the pintles and at the five positions in this plane shown in figure 3. Radius readings were taken before the test was started and after the test was completed. The difference between the readings at any of the five positions was the change in radius for that position. The dial gages were graduated to 0.001 in., and readings were estimated to 0.1 division. Readings at any position generally checked each other within 0.3 or 0.4 of a division as the specimens were removed from and again placed in the V blocks between readings.

III. PROGRAM OF TESTS

In a preliminary investigation of this kind it seemed impractical before the tests were started to decide definitely upon the whole program. As the tests progressed, a consideration of the results available at the time governed the conditions for the later tests. The program of tests as the investigation was carried out may be considered as divided in three series of tests. The materials used and the conditions of test are given under the discussion of results in tables 2, 3, and 4.

In the tests of series A, different combinations of materials for pintles and cups were used. The tests were made under a pressure of 2,000 lb/in.^{2}, the pintle bearings were not lubricated, and the cups were ungrooved.

The tests of series B were also made under a pressure of 2,000 lb/in^2. The tests of series B were made for the purpose of comparing the wearing life of cups without grooves with those in which two grooves, about ⅛ in. wide and 1/16 in. deep, were cut along meridian circles of the hemispherical bearing surface at right angles to each other, one of the grooves being in the plane of the lines of thrust. A vertical hole was drilled in the cup and a vertical hole and a horizontal hole were drilled in the threaded plug, as shown by the dotted lines of figure 1, so that water circulation over the bearing surfaces or at least through the grooves was possible for test 18. For the comparison of ungrooved cups and grooved cups with lubrication, a plain compression grease cup, holding about 1 cubic inch, was screwed into the vertical hole of the cup plug as shown in figure 1, and the horizontal water circulation hole was closed. A pressure of about 50 lb/in.^{2} on the lubricant was obtained by screwing the cover of the grease cup by hand.

The cups in the tests of series C were grooved and the bearings were lubricated as indicated in table 3, the tests being made with greater bearing pressures than were used in the other series.

An attempt was made to use greater pressures than are given in table 3 for series C, but the motor driving the pintle supports did not have sufficient power.

IV. RESULTS AND DISCUSSION

1. CHEMICAL COMPOSITION OF MATERIALS

The chemical composition of the materials used for pintles and cups is given in table 1.

TABLE 1.—*Chemical composition of materials used for pintles and cups*

Material	Analysis furnished by	C	Mn	S	P	Si	Ni	Cr	Mo	Cu	C	Fe	Al	Sn	Zn	Pb
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Aluminum bronze	NBS	----	0.11	----	----	----	5.0	----	----	80.0	----	5.2	9.2	0.14	0.25	----
Chromium steel	WD	0.14	.40	0.016	0.013	0.32	----	5.15	0.50	----	----	----	----	----	----	----
Malleable cast iron	M	2.4 to 2.6	.40 to .55	.04 to .08	.15 to .19	1.9 to 2.1	----	----	.3 to .4	.8 to 1.0	0.6 to 0.8	----	----	----	----	----
Monel:																
H-Monel	M	.10	.50	.020	----	1.25	61.00	----	----	34.0	----	2.75	----	----	----	----
K-Monel	M	.16	.50	.005	----	.20	65.00	----	----	27.0	----	1.50	3.45	----	----	----
M-Monel	M	.15	1.10	.010	----	.10	67.00	----	----	28.0	----	1.70	----	----	----	----
S-Monel	M	.10	.50	.020	----	3.50	60.00	----	----	33.0	----	2.75	----	----	----	----
Nickel steel	WD	.36	.65	.022	.031	.21	3.43	----	----	----	----	----	----	----	----	----
Nickel-chromium steel	WD	.38	.55	.025	.024	.15	3.28	1.31	----	----	----	----	----	----	----	----
Phosphor bronze	NBS	----	----	----	.46	----	----	----	----	80.2	----	----	----	10.9	----	8.3
Stainless steel A	M	.12 max	.40 to .50	.025 max	.025 max	.50 max	----	12 to 15	.50 max	----	----	----	----	----	----	----
Stainless steel B	M	.08 to .20	.40 to .50	.025 max	.025 max	.50 max	7 to 9	17 to 19	----	----	----	----	----	----	----	----

NBS=National Bureau of Standards.
WD=War Department.
M=Manufacturer.

2. TESTS OF SERIES A—DIFFERENT COMBINATIONS OF MATERIALS

Table 2 gives the results of the tests of series A. The change in radius measurements for the tests of series A are given to an enlarged scale in figure 7. The pintles and cups for tests 1 to 6, inclusive, are shown after test in figure 8. The pressure of 2,000 lb/in.^{2} was evidently great enough to produce failures, i. e., operation of the circuit breaker on the driving motor, in some of the pintle bearings with a small number of cycles. Failure in each case was due to excessive wear or to scoring. It appeared from an examination of the specimens that the failure was due to the material in the cup rather than in the pintle. In fact, the only satisfactory tests were those for which phosphor bronze was used as the cup material. Tests were not made with phosphor bronze as a pintle material.

TABLE 2.—*Results of accelerated-service tests of pintle bearings—series* A

Different combinations of materials; pressure 2,000 lb/in.^{2}; cups ungrooved; pintle bearings not lubricated

Test	Pintle material	Cup material	Cycles	Description of bearing after test
1	Nickel steel	Phosphor bronze	225,300	Pintle and cup slightly scored. Very little wear.
2	do	Aluminum bronze	1,100	Pintle and cup scored badly.
3	Stainless steel A	Stainless steel B	400	Do.
4	Chromium steel	Chromium steel	200	Do.
5	do	Nickel-chromium steel	100	Do.
6	Nickel steel	Malleable cast iron	100-	Do.
7	K-monel	S-monel	100-	Pintle and cup scored slightly.
8	M-monel	do	100-	Do.
9	S-monel	H-monel	100-	Pintle and cup scored badly.
10	do	S-monel	100-	Do.
11	Stainless steel A	H-monel	100-	Do.
12	do	S-monel	118	Do.
13	H-monel	Phosphor bronze	290,400	No failure.
14	K-monel	do	273,000	Pintle and cup scored slightly.
15	M-monel	do	400,800	No failure.
16	S-monel	do	288,000	Do.

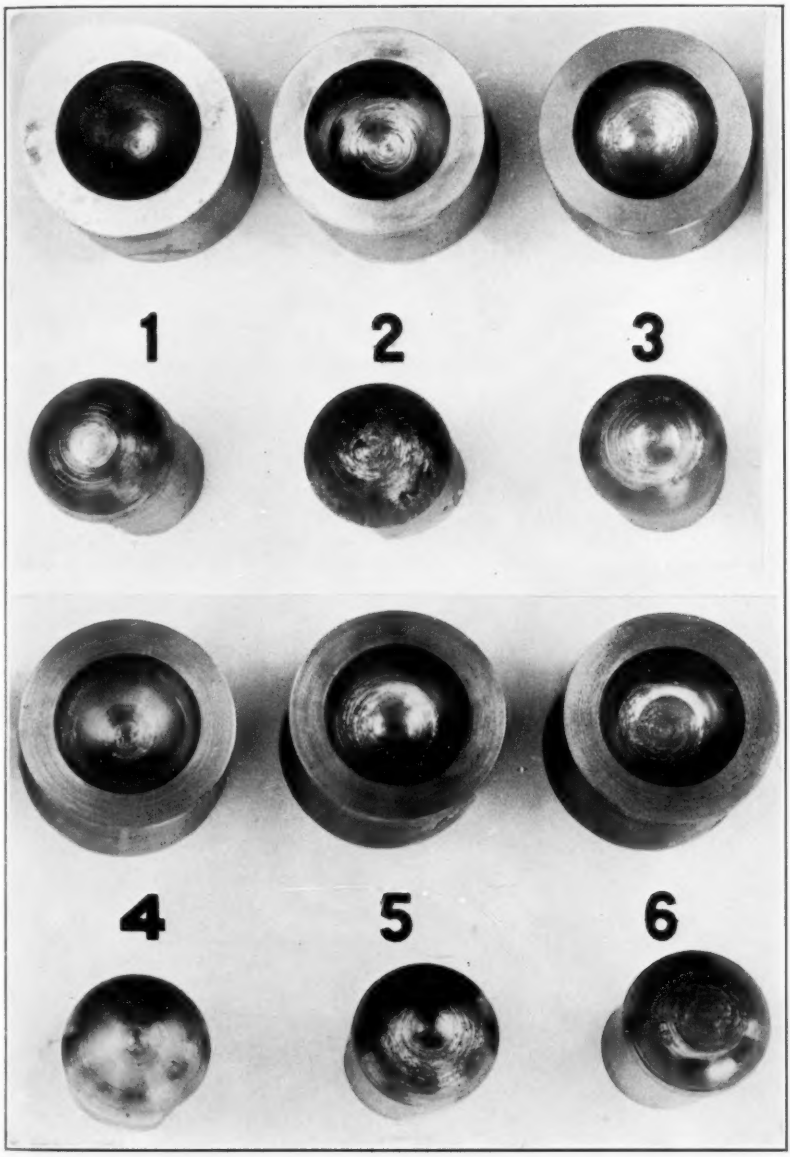

FIGURE 8.—*Pintles and cups after test, during which a pressure of 2,000* lb/in.^{2} *was maintained.*

The numbers 1 to 6 show the sequence of tests and the corresponding numbers of the specimens.

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Table 2 shows that when phosphor bronze was not used for the cup material, scoring occurred at a very small number of cycles for the steels, the cast iron, and the monel metal. The aluminum-bronze cup was worn excessively.

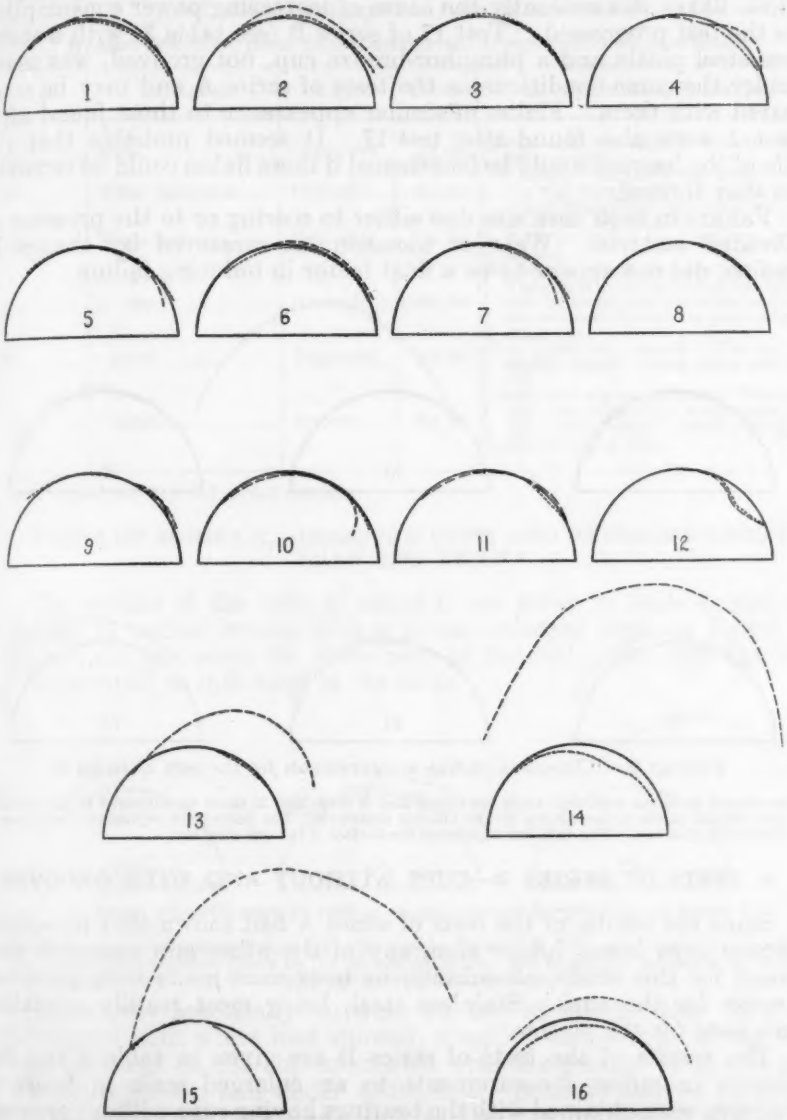

FIGURE 7.—*Change in radius measurements for the tests of series* A.

The change in radius measured along the radial lines is magnified 25 times as compared to the radius of the original pintle surface shown by the full-line semicircle. The dotted line represents the surface of the pintle after test. The dash line represents the surface of the cup after test.

The power required for the tests of the pintles of monel metal with phosphor-bronze cup (tests 13, 14, 15, and 16) was greater than for test 1, in which nickel steel was used as the pintle material. The pintle materials, H-monel, M-monel, and S-monel, with phosphor

bronze cups not grooved and the bearing not lubricated, were the only ones tested under a pressure of 2,000 lb/in.^{2} which withstood as many as 288,000 cycles.

At the completion of test 1, black metallic flakes were found between the phosphor bronze and the nickel steel. The presence of these flakes was evidently the cause of increasing power consumption as the test progressed. Test 17 of series B (see table 3) with a stainless-steel pintle and a phosphor-bronze cup, not grooved, was made under the same conditions as the tests of series A and may be compared with them. Flakes of similar appearance to those found after test 1 were also found after test 17. It seemed probable that the life of the bearing would be lengthened if these flakes could be removed as they formed.

Failure in each case was due either to scoring or to the presence of abraded material. Wear or abrasion, as measured by change in radius, did not appear to be a final factor in inducing failure.

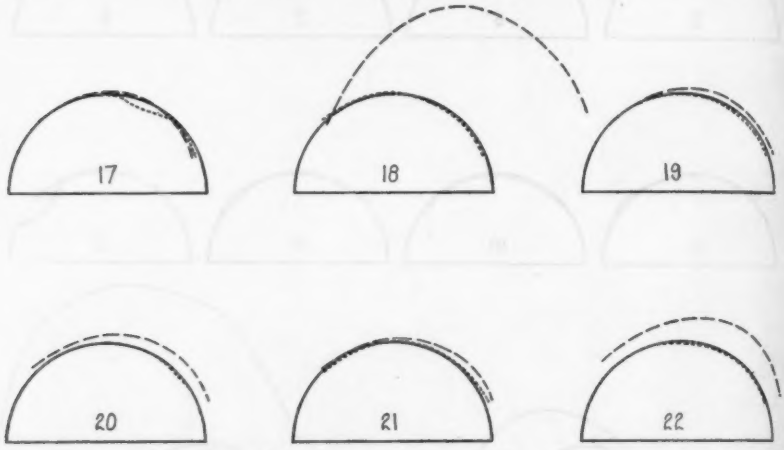

FIGURE 9.—*Change in radius measurements for the tests of series B.*

The change in radius measured along the radial lines is magnified 25 times as compared to the radius of the original pintle surface shown by the full-line semicircle. The dotted line represents the surface of the pintle after test. The dash line represents the surface of the cup after test.

3. TESTS OF SERIES B—CUPS WITHOUT AND WITH GROOVES

Since the results of the tests of series A had shown that phosphor-bronze cups lasted longer than any of the other cup materials proposed for this study, all subsequent tests were made with phosphor bronze for the cups. Stainless steel, being most readily available, was used for the pintles.

The results of the tests of series B are given in table 3 and the change in radius measurements to an enlarged scale in figure 9. Failures were obtained with the bearings having cups without grooves, but none was obtained with cups having grooves and tested at the 2,000 lb/in.^{2} pressure. The number of cycles, upward of 400,000, to which each of the three combinations having grooved cups was subjected, indicates that the water circulation, white-lead lubrication, or grease lubrication would give satisfactory service at this pressure, provided valid conclusions may be drawn from the results

of these short-time tests. The results of test 19 show that cups without grooves and with white lead as a lubricant lasted for more than 288,000 cycles.

TABLE 3.—*Results of accelerated service tests of pintle bearings, with ungrooved and with grooved cups and lubrication—series* B

[Pressure 2,000 lb/in.²; pintles made of stainless steel A; cups made of phosphor bronze]

Test	Lubrication	Cups	Cycles	Description of bearing after test
17	None	Ungrooved	103,000	Pintle and cup slightly scored. Black flakes present.
18	Water circulation	Grooved	405,300	No failure. The pintle was smooth. The cup was worn so that the groove in the area of direct thrust was nearly worn out.
19	White lead	Ungrooved	318,000	Pintle and cup slightly scored. Black flakes had closed the lubrication hole in the cup.
20	do	Grooved	1,000,700	No failure. Pintle and cup were smooth. The groove in the thrust area was bridged over by bronze and the white lead could not be forced through the grooves by the grease cup.
21	* grease	Ungrooved	156,000	The pintle was smooth. The cup was slightly scored. Black flakes were present.
22	* grease	Grooved	844,700	Pintle and cup were smooth. The grease cup was filled three times during the test. Grease could be forced through the grooves at any time.

* With lead-soap base and asphalt content.

4. TESTS OF SERIES C.—GROOVED CUPS AND PRESSURE GREATER THAN 2,000 LB/IN.²

The results of the tests of series C are given in table 4, and the change in radius measurements to an enlarged scale in figure 10. Failure did not occur for these tests at 288,000 cycles, but the tests were stopped as indicated in the table.

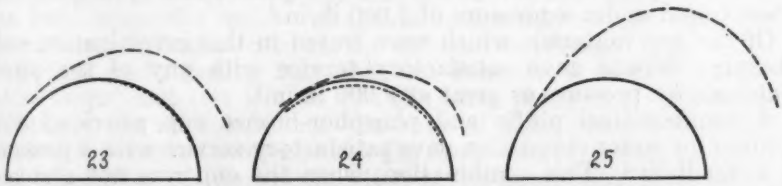

FIGURE 10.—*Change in radius measurements for the tests of series* C.

The change in radius measured along the radial lines is magnified 25 times as compared to the radius of the original pintle surface shown by the full-line semicircle. The dotted line represents the surface of the pintle after test. The dash line represents the surface of the cup after test.

There was practically no wear on any of the pintles. The cup lubricated with white lead showed, roughly, one-quarter of the wear that occurred on the cup lubricated with the grease. The cup with water circulation and under 4,000 lb/in.² pressure showed relatively little wear, about twice as much as the cup lubricated with white lead and tested with the 6,000 lb/in.² pressure.

TABLE 4.—*Results of accelerated service tests of pintle bearings, with grooved cups, lubrication, and large bearing pressures—series* C

[Pintles made of stainless steel; cups made of phosphor bronze]

Test	Lubrication	Pressure	Cycles	Description of bearing after test
		lb/in.²		
23	Water circulation	4,000	301,400	No failure. Pintle and cup were slightly scored. The grooves in the cups were full of bronze flakes.
24	White lead	6,000	290,200	No failure. Pintle and cup were not scored. The groove in the thrust area of the cup was bridged over by bronze and the white lead could not be forced through the grooves by the grease cup.
25	[a] Grease	6,000	336,900	No failure. Pintle and cup were not scored. The groove in the thrust area of the cup was bridged over by bronze, but the grease could be forced through the grooves at any time during the test.

[a] With lead-soap base and asphalt content.

Tests were attempted with the monel alloys as pintles and pressures greater than 2,000 lb/in.² The motor driving the pintle support did not, however, have sufficient power to drive the pintle support with these higher pressures.

The results of tests 13, 14, 15, and 16 (table 2) with monel-metal pintles were more satisfactory than for test 1, nickel-steel pintle (table 2) or for test 17, stainless-steel pintle (table 3) at a pressure of 2,000 lb/in.²

V. SUMMARY AND CONCLUSIONS

Pintles of H-monel, M-monel, and S-monel, used with phosphor-bronze cups not grooved and with the pintle bearing not lubricated were the only pintle materials investigated which withstood as many as 288,000 cycles (the number of cycles expected in 20 years' service) when tested under a pressure of 2,000 lb/in.²

Of the cup materials which were tested in this investigation only phosphor bronze gave satisfactory service with any of the pintle materials for pressure as great as 2,000 lb/in.²

A stainless-steel pintle and phosphor-bronze cup provided with grooves for water circulation gave satisfactory service with a pressure of 4,000 lb/in.² This combination, when the cup was not grooved, did not withstand 288,000 cycles at the lower pressure of 2,000 lb/in.²

Satisfactory service with pressures as high as 6,000 lb/in.² was obtained by using stainless-steel pintles and phosphor-bronze grooved cups lubricated with either white lead or a grease having a lead-soap base and asphalt content.

WASHINGTON, September 24, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP855

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ACCELERATED AGING TEST FOR WEIGHTED SILK

By Wm. D. Appel and Daniel A. Jessup

ABSTRACT

The rate at which silk, particularly weighted silk, will deteriorate on exposure to light, heat, and moist air cannot be predicted simply from the amount of weighting or other substances present on the silk. A laboratory test which will indicate the relative stability of silks is needed.

The aging, as revealed by changes in breaking strength, of a variety of silk and weighted-silk cloths when stored in the dark, when exposed to the daylight received through a north window (natural aging), or to the radiation from the glass-enclosed carbon-arc lamp under controlled conditions of temperature and relative humidity of the atmosphere (accelerated aging) was studied.

Data on the accelerated aging of some typical silk dress fabrics were obtained. An accelerated aging test is proposed.

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I. INTRODUCTION

It is well known that silk deteriorates when exposed to daylight, becoming weak and brittle, and that the rate of deterioration depends not only upon the nature of the radiation and of the atmosphere about the silk, but also upon the substances present on it. Sizing, weighting, and finishing materials and even traces of acids, alkalies, salts, soaps, and oils left on the silk after processing, drycleaning, or laundering may influence the rate of deterioration materially. Some of these substances increase the rate, others decrease it. Therefore the extent of the deterioration to be expected in a given time cannot be predicted simply from the *amount* of weighting or other substances present in the silk.[1]

[1] References to some of the experimental work on the deterioration of silk which can be cited in support of these statements follow:

M. Furry and R. Edgar, *A study of weighted silk fabric*, J. Home Econ. **20**, 901–905 (1928).

M. H. Goldman, C. C. Hubbard, and C. W. Schoffstall, *Effect of drycleaning on silks*. Tech. Pap. BS **20**, 605–634 (1926) T322.

M. E. Griffith, *The breaking and bursting strengths of some weighted and unweighted silk fabrics after exposure to light*, Ohio Agr. Expt. Sta. Bimonthly Bul. 151, 145–148 (1931).

M. Harris, *Photochemical decomposition of silk*, BS J. Research **13**, 151–155 (1934) RP697.

M. Harris and D. A. Jessup, *The effect of* pH *on the photochemical decomposition of silk*, BS J. Research **7**, 1179–1184 (1931) RP395.

K. Homolka, *Behandlung der Seide, um ihre Widerstandskraft gegen die Einwirkung des Lichtes zu erhöhen* Melliand Textilber. **6**, 584–585 (1925).

E. Ristenpart, *Die Wirkung des Lichtes auf erschwerte Seide*, Z. angew. Chem. **22**, 18–21 (1909).

N. M. Roberts and P. B. Mack, *A study of the effects of light and air on the physical properties of weighted and unweighted silks*, J. Home Econ. **24**, 151–165 (1932).

W. Stockhausen, *Beitrage zur Kenntnis der Seidenerschwerung*, Seide **34**, 445–448 (1929).

A. J. Turner, *The influence of atmospheric exposure on the properties of textiles*, J. Soc. Dyers Colourists **36**, 165–172 (1920).

L. Vignon, *Résistance de tissus aux intempéries et aux rayons ultraviolets*, Compt. rend. **170**, 1322–1324 (1920).

The deterioration can be accelerated in the laboratory by exposing the silk to radiation of relatively high intensity, rich in the shorter wave lengths and by increasing the temperature and relative humidity of the air about the silk. If the relative stability of silks in this accelerated aging is indicative of the relative stability under "natural" conditions, laboratory exposures can be utilized in the development of protective finishes, in the control of the finished product, and in the specification of silks with respect to relative stability. This last is of especial interest to distributors and users of weighted silks.

In order to compare natural and accelerated aging, a study was made of the changes in breaking strength of a variety of silk cloths when stored in the dark, when exposed to the daylight received through a north window, and when exposed to the radiation from the glass-enclosed carbon-arc lamp under controlled conditions of temperature and relative humidity of the atmosphere.[2] The results are given in this paper.

II. MATERIALS AND PROCEDURE

The silk cloths used for the preliminary experiments were all made from the same piece of commercially boiled-off cloth. Eight pieces of it were prepared in different ways in mills regularly engaged in this work. One piece was the original boiled-off silk. A second piece was dyed, "pure dye" in the figures. Six pieces were weighted to different extents and dyed. The series of eight pieces thus prepared is designated "dyed." A portion of each of the cloths of the dyed series was printed. A second portion of each of the cloths was "discharge printed."

The silk cloths used for the confirmatory experiments were similar to those of the dyed series, just described, but were made from a different piece of silk cloth. Two sets were prepared, the boiling-off, weighting, and finishing being done in two different mills.

Each sample of cloth for natural aging was divided into two pieces. One piece was stored in the dark in a clothes locker. The other was hung in one of the large factory-type windows of the cotton mill at the National Bureau of Standards. The samples were placed about four feet from the north windows and were exposed continuously. All samples in the preliminary tests were exposed simultaneously and all in the confirmatory tests simultaneously. The samples were frequently interchanged in position in order, as far as possible, to ensure comparability of exposure. The breaking strength of each sample in the warp direction was determined at intervals of time by the 1-inch strip method, averaging the results of three breaks. All samples were conditioned and tested in an atmosphere of 65-percent relative humidity having a temperature of 70° F (21° C).

The temperatures in the storage locker and in the window where the samples were exposed were observed three times daily during the

[2] Although the aging of silk cloth is not fully represented by changes in breaking strength, this seemed to be the simplest criterion to use for these exploratory studies. The changes in elongation at break of the fabrics were determined, but the results were somewhat erratic and are not reported.

first month and the last two weeks of the preliminary aging tests. The average temperature in the locker was 28° C and in the window 31° C during the first month. During the last two weeks the average temperature in the locker was 22° C and in the window 32° C. Thus the stored samples were at a lower temperature than the exposed.

The relative humidity of the atmosphere in the locker was that of the ordinary office room in which it was kept. The relative humidity of the atmosphere about the exposed samples was maintained at 70 to 75 percent during a considerable part of the time when the room was being used for spinning.

Accelerated aging was obtained by placing the samples in an insulated box having a glazed window, facing the glass-enclosed carbon-arc lamp of the Fade-Ometer.[3] The temperature of the air in the box was maintained at either 55 or 67° C by a thermostat, and the relative humidity was maintained at either 30 or 75 percent with saturated solutions of magnesium chloride and sodium chloride, respectively.[4] A motor-driven propeller kept the air in the box well mixed.

III. AGING OF SILK UNDER NATURAL CONDITIONS

The aging indicated by changes in breaking strength of silk cloth finished in 24 different ways, in dark storage and in the radiation received through a north window, is shown in figure 1. None of the fabrics decreased in strength more than 20 percent when stored in the dark for 240 days and the strength of the more heavily weighted silks did not change more than that of the silks containing less weighting or no weighting. The decrease in strength on exposure to light for 240 days varied from a little over 20 percent to over 95 percent, depending upon the finishing treatment the silk had received. In general, the discharge printed fabrics decreased in strength to a greater extent in a given time than the corresponding printed or dyed fabrics. The fabrics containing the greatest amounts of weighting did not decrease in strength as rapidly as did some of the fabrics containing less weighting. There was no consistent relationship between the decrease in breaking strength of these fabrics and the amount of nonfibrous materials in them.

IV. ACCELERATED AGING OF SILK

The changes in breaking strength of the 41-percent weighted, dyed silk referred to in figure 1, when exposed to the radiation of the glass-enclosed carbon-arc lamp under different conditions of intensity of radiation, relative humidity, and temperature of the atmosphere, are

[3] Manufactured by the Atlas Electric Devices Co., Chicago, Ill. Arc voltage 140, direct current, 13 amperes.

[4] Hugh M. Spencer, *Laboratory methods for maintaining constant humidity*, Int. Crit. Tables, **1**, 67 (1926).

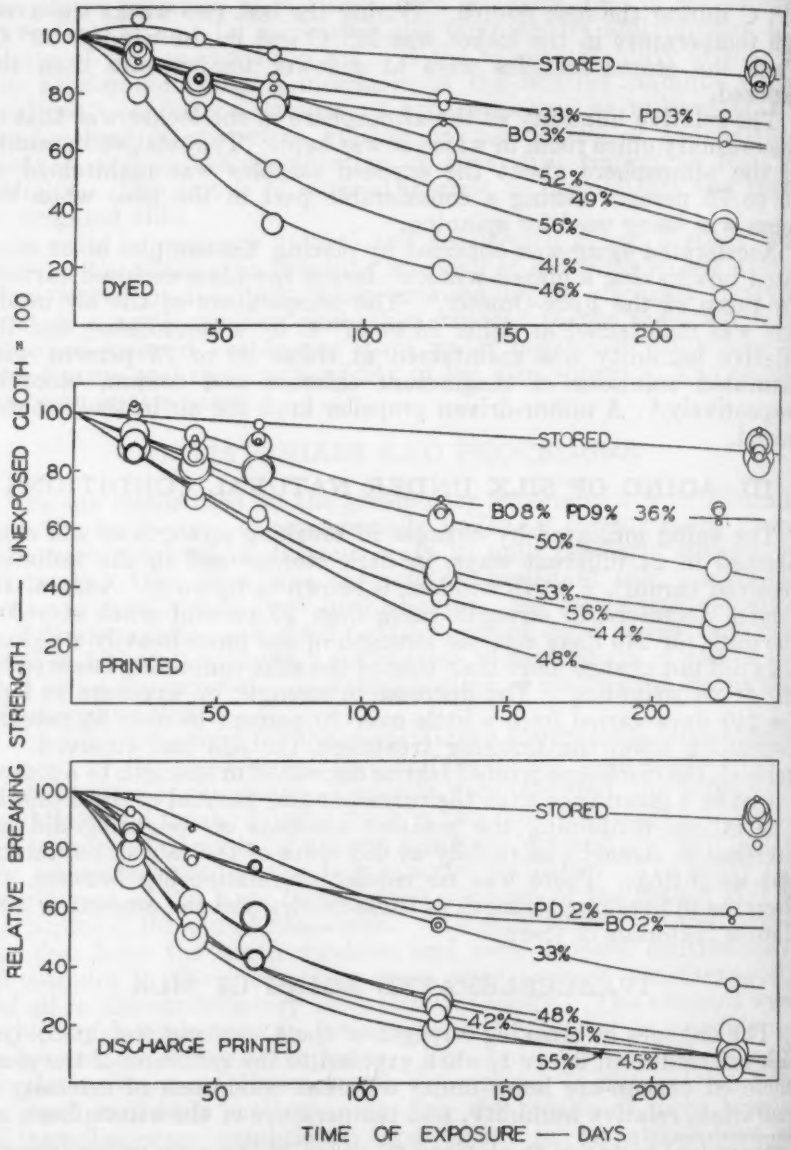

FIGURE 1.—*Change in breaking strength of silk cloths when exposed to diffused daylight and stored in the dark.*

All cloths were made from the same piece of boiled-off cloth. The "dyed" series (upper chart) included a piece of the original boiled-off silk (BO), another piece dyed, but not weighted (PD), other pieces weighted to different extents and dyed. The "printed" series (middle chart) and "discharge printed" series (lower chart) included portions of each of the cloths in the dyed series, which were either printed or discharge printed. The percentages given indicate the total amount of weighting and/or other nonfibrous constituents of the finished fabrics (dry basis).

shown in figure 2. The radiation received by the fabric passed through window glass ⅛ inch thick as well as the glass globe of the arc. The distance from arc to cloth was 15 inches for intensity 1.0 and 49 inches for intensity 0.1. The fabric required about twice as long an exposure at the lower intensity as at the higher to produce the same change in breaking strength. A change in relative humidity from 30 to 75 percent and in temperature from 55 to 67° C each materially decreased the time required to produce a given change in the breaking strength of the fabric. The breaking strength decreased about as much when the fabric was exposed for 20 hours at intensity 1, relative humidity 75 percent, and temperature 55° C as when it was exposed for 240 days in the north window.

V. COMPARISON OF NATURAL AND ACCELERATED AGING

The experiments just described were repeated with two new series of fabrics in order to confirm the results. The natural and accelerated aging of some of these fabrics are compared in figures 3 and 4.

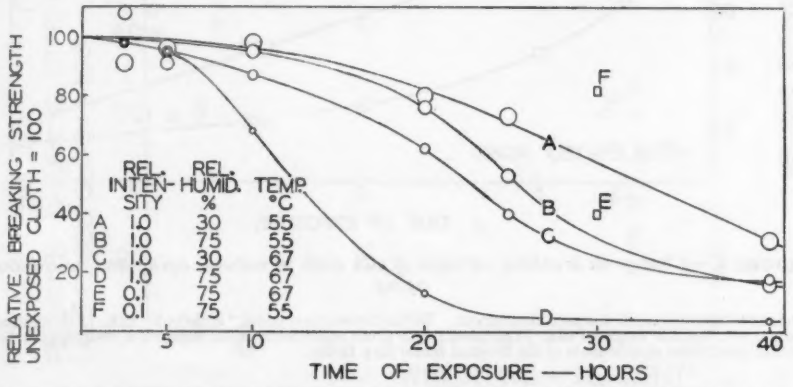

FIGURE 2.—*Change in breaking strength of weighted silk cloth when exposed to the radiation of the glass-enclosed carbon-arc lamp under controlled conditions of intensity of radiation, relative humidity and temperature of the atmosphere.*

The cloth was the dyed silk containing 41 percent weighting, figure 1.

The strengths of the boiled-off, pure dye, 51-, 53-, and 56-percent weighted silks finished in one mill (fig. 3) decreased very slowly and at about the same rate in the natural aging; the strength of the 42-percent weighted decreased distinctly faster, and that of the 38-percent weighted very much faster. Similar results were obtained with these fabrics in the accelerated aging test as shown in figure 3.

The strengths of the fabrics which were finished in a second mill did not decrease at a rapid rate in either the natural or the accelerated aging, except toward the end of the tests. Then the 45-percent weighted silk began to weaken rapidly in the natural aging and apparently also in the accelerated aging (fig. 4).

The results indicate general agreement in the behavior of silk fabrics in the natural aging and accelerated aging under the conditions specified when judged by the change in breaking strength. The relative behavior in the natural aging is reproduced in the accelerated aging as well as may be expected for a test of this kind.

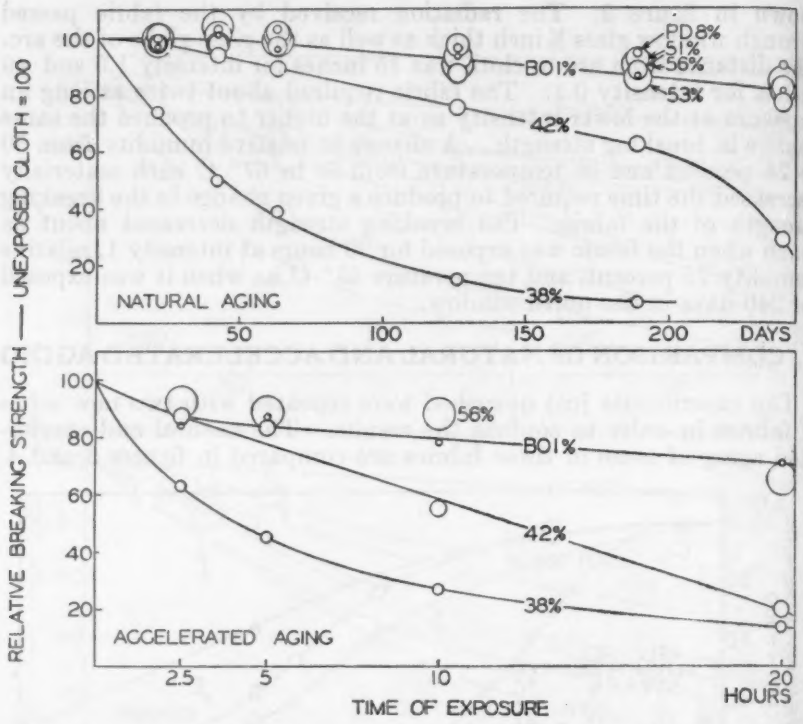

FIGURE 3.—*Change in breaking strength of silk cloth in natural aging and accelerated aging.*

The same basic silk cloth was used throughout. BO indicates the original "boiled-off" silk. PD indicates the dyed, but not weighted silk. The percentages given indicate the total amount of weighting and/or other nonfibrous constituents of the finished fabric (dry basis).

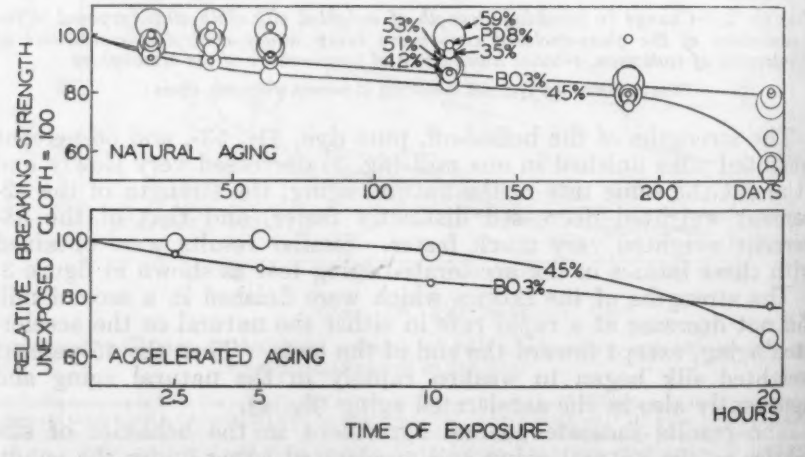

FIGURE 4.—*Change in breaking strength of silk cloth in natural aging and accelerated aging.*

The same basic cloth as that represented in figure 3 was used. Portions of it were dyed and finished by a different finishing plant than the one which finished the cloths of figure 3. The notation used in figure 3 applies to this figure as well.

VI. ACCELERATED AGING OF TYPICAL DRESS FABRICS

Through the cooperation of the American Home Economics Association and students of home economics in colleges in different parts of the country, samples taken from 23 silk dress fabrics purchased during the spring of 1930 for use in dressmaking projects were subjected to the accelerated aging test. Some of the results are given in figure 5.[5] The pure dye,[6] as well as the weighted silks, varied considerably in their relative stability in the test, judged by change in breaking strength. Nine out of the ten pure-dye silks in the lot had more than 50 percent of their original strength (warp or filling depending upon which showed greater change) after the 20-hour exposure. Only 4 of the 13 weighted silks had more than 50 percent of their original strength after exposure. The two silks containing about 35-percent weighting were among the four least stable of the

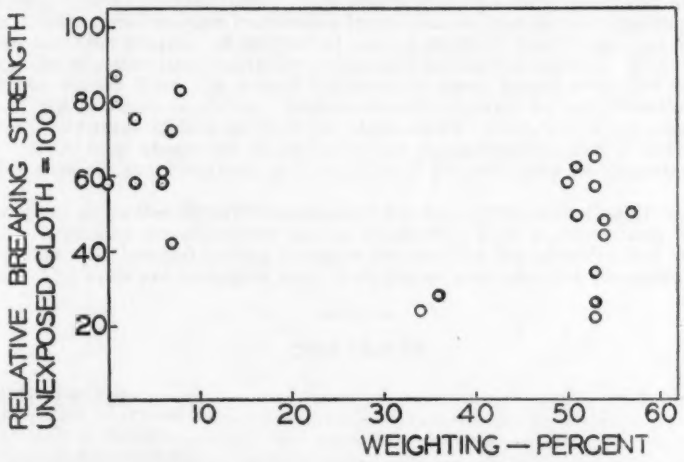

FIGURE 5.—*Typical silk dress fabrics—breaking strength after accelerated aging in relation to the amount of weighting or other nonfibrous materials present.*

weighted silks and were distinctly inferior to 8 weighted silks containing 50-percent weighting or more. The stability of neither pure dye nor weighted silks bore any relation to the weight per square yard. The most stable of the pure dye silks weighed 0.75 oz/yd ^{2} yard and the least stable 1.34 oz/yd ^{2}.

VII. PROPOSED ACCELERATED AGING TEST

The aging test outlined below is proposed on the basis of the results obtained in this study. It is hoped that, through the application of this test to a large number of fabrics of known serviceability by laboratories regularly engaged in testing silk fabrics, the relative stabiliy required for various uses can be worked out.

Specimens of the cloth suitable for warp and filling breaking-strength tests are exposed for 20 hours to the radiation from a glass-enclosed

[5] Detailed information concerning the constructions and properties of these fabrics is being incorporated by Dr. R. K. Worner of this Bureau in a report on the serviceability of dresses made from the fabrics.
[6] Silk containing less than 10 percent of nonfibrous materials. See Federal Trade Commission "Statement by the Commission, Trade Practice Conference, Silk Weighting" of June 18, 1932.

carbon-arc lamp, such as that of the Fade-Ometer, operated on direct current of approximately 13 amperes with the voltage across the arc approximately 140 volts. The distance from the specimens to the center of the arc is 15 inches. The specimens are enclosed in a cabinet glazed with window glass approximately ⅛ inch thick between the specimens and the arc. The air in the cabinet is maintained at 75 to 77 percent relative humidity and 63 to 67° C. The breaking strength of the cloth after exposure, expressed as a percentage of the breaking strength before exposure in the direction, warp, or filling, showing the greater change in strength, is taken to be indicative of the probable relative stability of the fabric with respect to exposure to light, heat, and moist air.

WASHINGTON, October 4, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP856

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UNICONTROL RADIO RECEIVER FOR ULTRA HIGH FREQUENCIES USING CONCENTRIC LINES AS INTERSTAGE COUPLERS

By Francis W. Dunmore

ABSTRACT

A new type of radio receiver for frequencies between 100 and 300 megacycles per second (Mc/s) is described. This receiver differs from previous designs in that it utilizes quarter-wave concentric transmission lines as coupling impedances between amplifier stages. A method of using a single line per stage and means for varying the effective line length for unicontrol tuning are shown. The deviation of the line length from the actual full-quarter wave length over the frequency range of the receiver is given. Measurements showed an amplification of the order of 2 per stage at 300 Mc/s, 6 per stage at 200 Mc/s, and 9 per stage at 175 Mc/s. With four stages of radio-frequency amplification and a detector, an effective over-all amplification of the order of 100,000 may be expected at 200 Mc/s.

The paper gives the circuit arrangement for a receiver consisting of four stages of radio-frequency amplification and a detector. This receiver uses four concentric lines with ganged tuning plungers for varying the effective line lengths in unison. The lines are arranged with their major axes about a common center.

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I. INTRODUCTION

The ultra high radio frequencies (above 30 Mc/s) are daily finding new applications. There is therefore increasing need for receivers designed to function at these frequencies. This paper describes the development of a radio receiver for these frequencies which differs from previous designs in that it utilizes quarter-wave concentric transmission lines grounded at one end as coupling impedances between amplifier stages. The theory and possibilities of concentric lines for such purposes were treated in an article in The Electrical Engineer by F. E. Terman.[1] This paper will therefore deal only with the special features and operating characteristics of this receiver.

[1] *Resonant lines in radio circuits*, Elec. Eng. **53**, no. 7, 1046–1053 (July 1934).

II. PRINCIPLE OF OPERATION

The use of quarter-wave lines as interstage coupling impedances is shown in figure 1 (a). A is a quarter-wave concentric line made up of an outer tubing B and an inner tubing C. B is grounded. C is connected to the plate of the electron tube G and is insulated from ground for direct current, but its lower end is grounded for radio frequency by means of plunger P, which is in metallic contact with C and capacitively connected to B. When the transmission line A is adjusted by moving plunger P to be some length less than a quarter of the wave length of the voltage impressed on the grid of tube G (the length is always shorter than $\lambda/4$ because of the capacitance of the plate in tube G, connecting leads, and circuit elements), a maximum voltage is built up in the plate circuit of tube G and

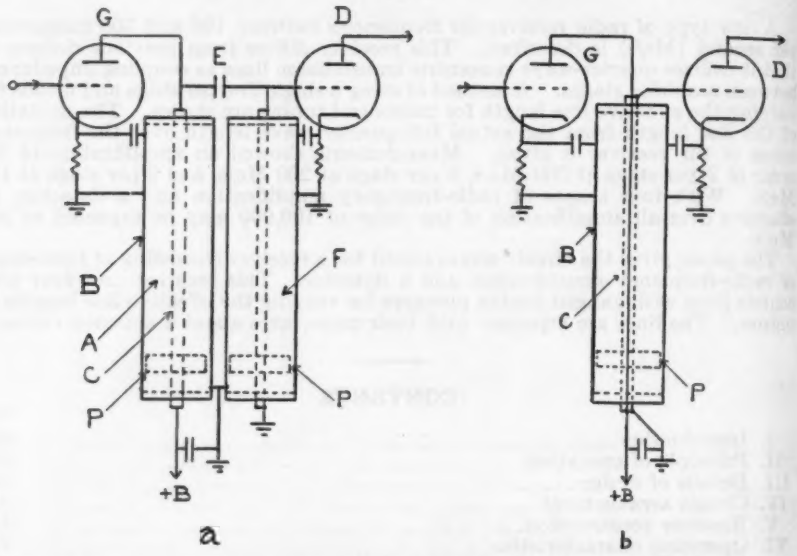

FIGURE 1.—*Concentric transmission line as an interstage coupling impedance.*

passed on through coupling condenser E to the grid of the second electron tube D. The grid of this tube is grounded for direct current, but is held at the radio-frequency voltage delivered to it by means of a second concentric line F similarly tuned to nearly a quarter wave length. With this type of coupling it is possible more nearly to match tube impedances and thereby obtain greater amplification per stage at ultra high radio frequencies than by other means.

Instead of a transmission line both in the output and in the input of each electron tube as shown in figure 1 (a), it is possible to reduce the number of lines by one-half by using a single line for both output and input circuits. This is made possible as shown in figure 1 (b) by running the insulated direct-current plate supply lead down through the center of the inner concentric line. In this way the plate of electron tube G is supplied with its proper direct current voltage without grounding it with respect to the radio frequency. The capacitance of this plate lead to the central concentric line C, takes the place of condenser E (fig. 1 (a)) and provides unity coupling

at the ultra high radio frequencies used, so that the radio-frequency voltage in the plate circuit of tube G is readily transferred to the central concentric line and thence to the control grid of tube D. The grid of electron tube D is grounded as before for direct current but held at the radio-frequency voltage delivered to it from electron tube G due to the high impedance built up when the line is tuned with plunger P.

III. DETAILS OF DESIGN

In order to obtain maximum efficiency, between frequencies of 100 and 300 Mc/s, from an amplifier using concentric lines as interstage coupling impedances, the concentric lines should be arranged so that all high-frequency connecting leads are as short as possible and arranged to have a minimum of capacitance to ground. This arrangement of lines should also be such as to facilitate their ganging for unicontrol operation. Each line should terminate in a separate shielding compartment. A convenient method of varying the effective line length is essential. This should be accomplished without introducing noise due to variable contacts or undue resistance in the line. The concentric lines should be made of copper or copper plated. The concentric line on the input should be provided with means for a proper impedance match to the antenna and associated transmission line. The receiver should of course be designed so that all wiring and parts are accessible and easily replaced.

IV. CIRCUIT ARRANGEMENT

The circuit arrangement of a receiver designed with the above facts in mind and incorporating a number of new features is shown in figure 2.

This receiver consists of four stages of radio-frequency amplification and a detector. A single concentric line per stage is used with the direct-current plate supply lead running down through the center line. The electrical length of each line is varied by means of a metallic plunger P, in contact with the central line but capacitively connected to the outer line in order to avoid noise due to variations in a friction contact. The plungers for a number of stages may all be controlled by insulated rods extending through the rear of the line and suitably ganged to give unicontrol tuning.

The transmission line tuning the grid of the input electron tube has a sliding contact A on the central line which connects to one side of the transmission line C coming from the antenna. In this way a better input impedance match may be realized.

The grid of each electron tube is grounded for direct current by connecting its low radio-frequency voltage end to ground. Grid bias is obtained with the usual cathode resistor properly bypassed.

The high-voltage end of each transmission line terminates in a separate shielding compartment containing a type 954 electron tube with associated wiring.

The detector circuit in this receiver was designed for detection at modulation frequencies in the broadcast radio-frequency band. The output terminal is therefore connected to the antenna terminal of a broadcast receiver and the resulting added amplification realized.

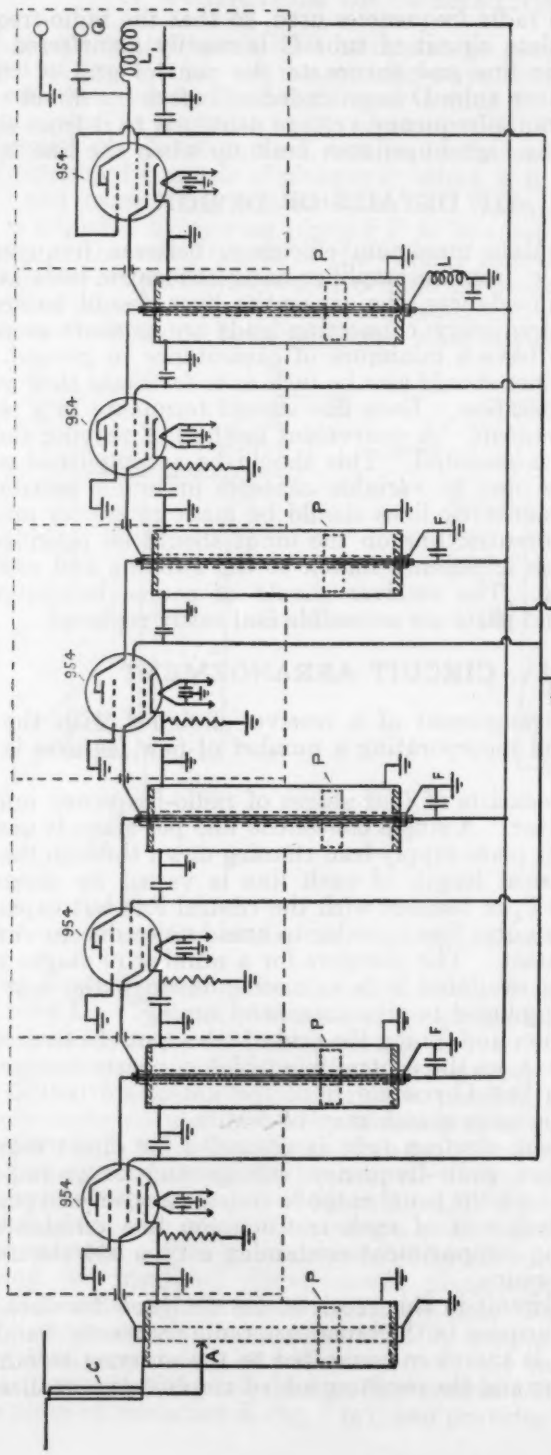

FIGURE 2.—*Circuit arrangement for a multistage ultra high radio-frequency amplifier using concentric line tuning.*

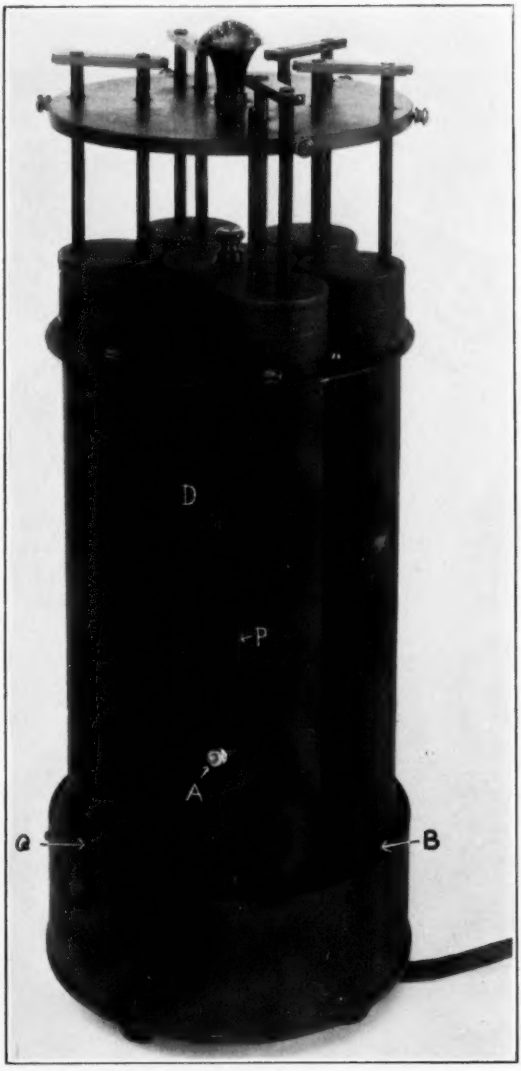

FIGURE 3.—*A four-stage concentric-line tuned radio receiver for 175* Mc/s *(1.71* m*) to 300* Mc/s *(1* m*).*

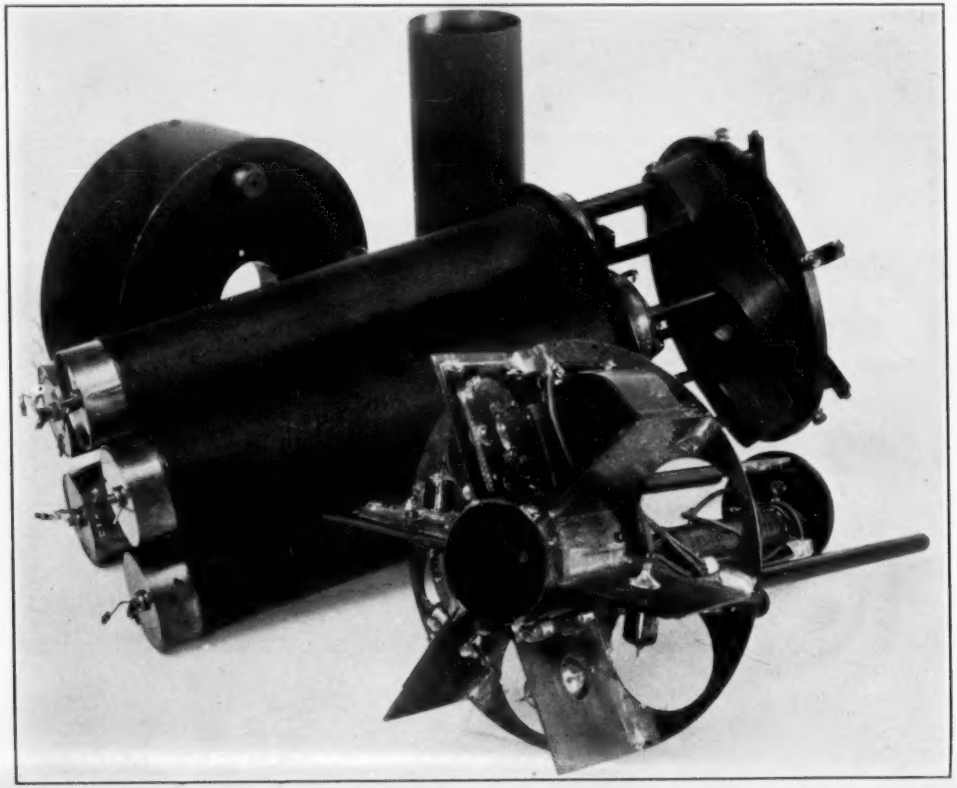

FIGURE 4.—*The concentric-line receiver showing method of assembly.*

The grid of the detector tube is held at the voltage of the modulated signal impressed on it by means of choke L in the low-voltage end of the transmission line. A similar choke L_1 in the plate circuit serves to deliver the modulation frequency to the output terminal. These chokes may be replaced by inductors tuned to the modulation frequency if desired, in which case the capacitance of the central line and plunger P to ground serve as part of the tuning capacitance for inductor L.

If the ultra high radio-frequency carrier has several radio-frequency modulations impressed upon it, these may all be obtained at terminal Q and received simultaneously on separate broadcast receivers connected to this terminal; or with a properly designed detector circuit and concentric lines designed to pass a band width of 2,000 kc/s, terminal Q may deliver a television signal if such a signal has been impressed on the ultra high radio frequency carrier.

V. RECEIVER CONSTRUCTION

Figures 3 and 4 show a receiver using the circuit arrangement shown in figure 2 and constructed in accordance with the design details mentioned in a previous paragraph. This receiver covers a useful frequency range of from 170 to 300 Mc/s (1.76 to 1.0 meters). The lower frequency limit is restricted only by the length of the transmission lines used. With but slight modifications longer lines may be inserted and the lower frequency limit thereby extended.

Figure 3 shows the receiver completely assembled. The five transmission lines are shown terminating at their lower ends in the circular shielding housing containing the separate shielded compartments for each line termination. The radio-frequency input terminals are shown at A and B. A makes contact through a slider operating on the central line of the input concentric line. (This is shown in detail in fig. 5.) Q is the output terminal which with its neighboring ground terminal is connected to the input of a standard broadcast receiver. The central cylinder D is merely a shield covering the voltage divider W (fig. 2) and associated wiring; it could also inclose a power pack if desired.

Each line contains a tuning plunger P attached to two bakelite rods extending through the upper ends of the lines. These rods are all attached to a common tuning control handle through a disk by means of set screws. By loosening the set screw on a given control rod that line may be tuned independently when desired. A suitable frequency scale (not shown) is attached to the disk. The third rod in the input transmission line is for operating the sliding contact attached to terminal A. The cap covering the upper end of cylinder D contains a terminal block where the B supply voltage is supplied to the upper end of each transmission line. The shielding cover on the top end of each transmission line covers the bypass condenser F shown in figure 2, and in the case of the last transmission line it contains the radio-frequency choke L in the detector grid to ground circuit.

FIGURE 4.—*The concentric-line receiver showing method of assembly.*

Figure 4 shows the receiver in a knockdown condition. This photograph shows how, with this type of assembly, the grid and plate leads to the electron tubes may be kept very short. These leads with tube clips attached may be seen on the left end of the transmission lines. One lead is fastened to an insulated wire running down through the hole in the central line (the plate lead) and the other (the grid lead) is attached to the central line.

The insulating disks holding the central line in position at the high-voltage end should have as little insulating material in them as possible, and this should be of high grade.

By loosening a few screws and taking the grid and plate clips from the electron tubes the receiver may be easily taken apart as shown.

In figure 5 is shown the type of transmission line used in the receiver. The one shown in this figure is used in the input circuit. It differs from the other four lines only in that it contains the sliding contact carrying the binding post A (see fig. 3 at A), and in that it does not contain the plate lead through the center line. The white pieces of paper held in slots in the tuning plunger are for insulating it from the outer line so as to prevent a direct metallic contact with resulting friction and noise. They are about 0.008 inch (0.02 cm) thick. This capacitance contact, so to speak, has an approximate capacity of 156 $\mu\mu$f and an impedance of 10 ohms at 100 Mc/s and 3.3 ohms at 300 Mc/s.

The outer conductor of each transmission line has an inside diameter of 4.6 cm and the inner conductor has an outside diameter of 0.49 cm. This ratio of 9.2 is the correct one according to Terman [2] to give maximum impedance.

Both inner and outer lines and plungers are of brass, copper plated.

VI. OPERATING CHARACTERISTICS

1. TRANSMISSION LINE LENGTHS

In figure 6 at A is shown the length of a quarter-wave line at different frequencies without external capacitance shunting the free end of the line.

When used as an interstage coupling impedance, however, each line has shunting it the capacitance of the plate of one type 954 electron tube and the grid of the following tube with associated leads. The total capacitance due to the electron tube elements is 6 $\mu\mu$f. The leads probably introduce an additional 3 $\mu\mu$f. The line length at resonance is therefore reduced accordingly, the line behaving as an inductance of such value as to form a parallel resonant circuit with the total shunting capacitance.

Curve B shows the calculated line lengths for different frequencies assuming the above shunting capacitance and a line surge impedance of 120 ohms.

Curve C shows the lengths as determined experimentally by tuning the receiver to each of the frequencies.

It will be seen from these curves that the electron tube and lead capacitance on the end of the transmission line have a marked effect in reducing the line length from a full quarter wave. In fact this reduction is some 73% at 300 Mc/s and 50% at 171.5 Mc/s, this percentage becoming progressively less as the frequency is lowered.

[2] F. E. Terman, *Resonant lines in radio circuits*, Elec. Eng. 53, no. 7, 1046–1053 (July 1934).

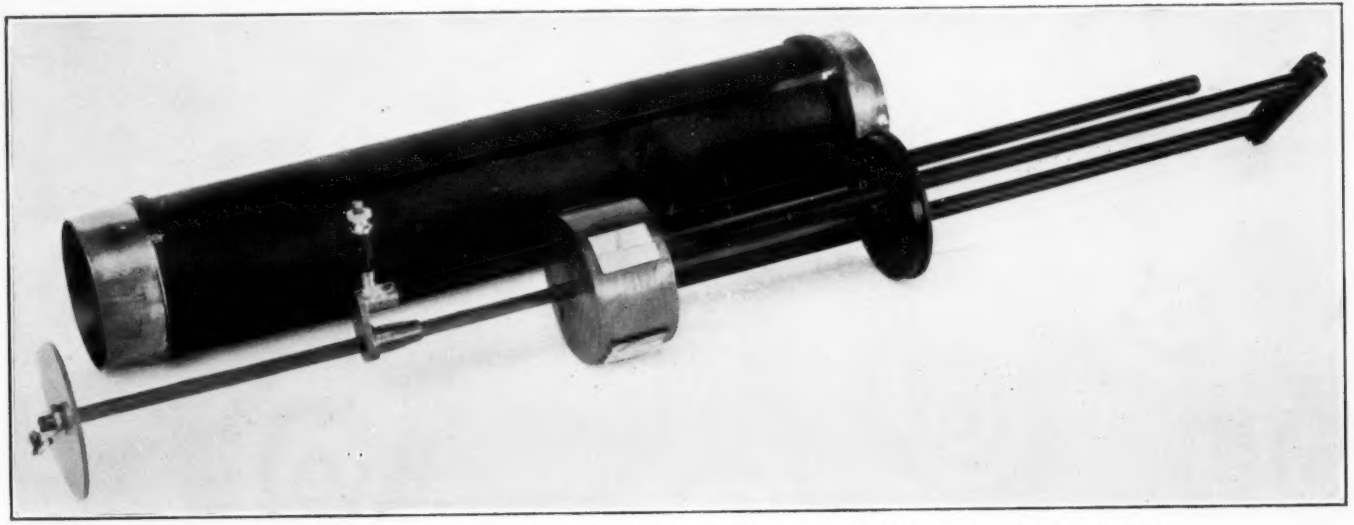

FIGURE 5.—*One of the concentric lines showing tuning plunger and sliding antenna input terminal.*

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The 100- and 140-megacycle points were obtained experimentally for curve C by temporarily replacing the line in the detector input circuit with one 50 cm long.

All concentric lines, except the input (which has only a grid element on its end), were found to be about the same length when the receiver was tuned to a given frequency. Variations in tube and lead capacitances made differences in length not over 1.0 cm. The input line is

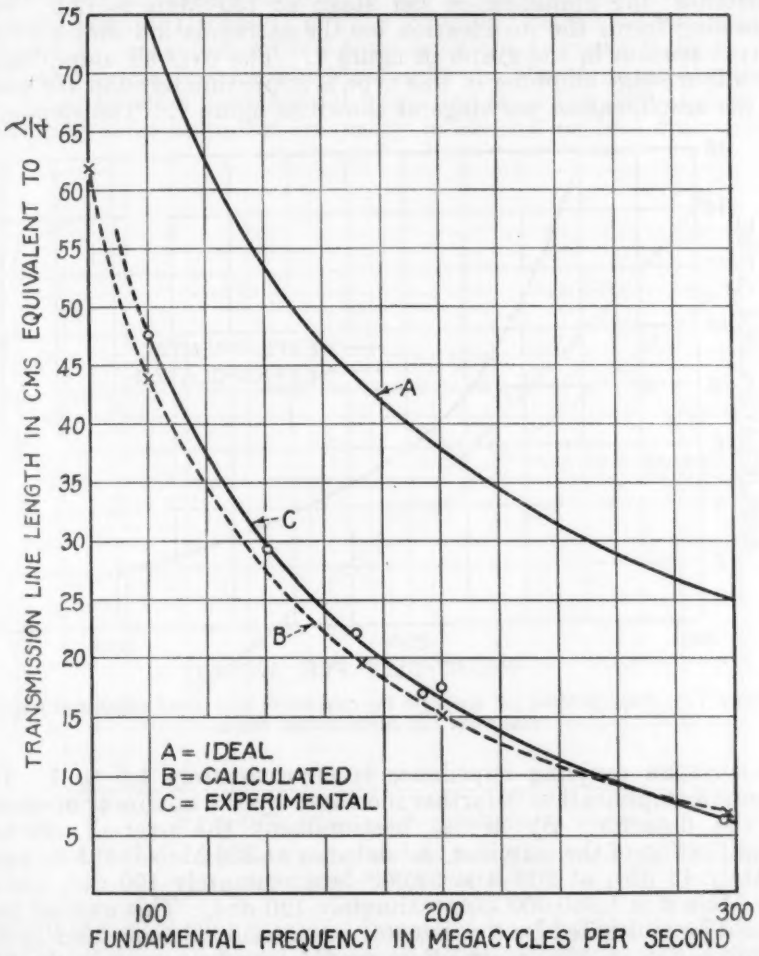

FIGURE 6.—*Transmission line length with and without capacitance of electron tubes and associated leads.*

some 2 to 4 cm longer than the others depending upon the position of contact A (fig. 2).

2. AMPLIFICATION PER STAGE

The amplification per stage as measured at different frequencies is shown in figure 7. From this graph and from the lengths of the concentric lines required for tuning to the different frequencies, the equivalent series resistance of the parallel resonant circuit formed by

the shunting capacitances and the concentric line used as an inductance may be computed. Assuming a tube amplification factor of 1,500 and a plate resistance of 1.5 megohms, the series resistance is 1.5 ohms at 300 Mc/s, 0.9 at 200 Mc/s, and 0.85 ohm at 171 Mc/s. From these values it may be assumed that the equivalent series resistance at 150 Mc/s is, say, 0.8 ohm. Computing backwards, on the basis of the same assumptions of amplification factor and plate-resistance, the amplification per stage at 150 Mc/s is 13.2. This reasoning forms the justification for the extrapolation shown by the dotted portion in the graph in figure 7. The over-all amplification for a four-stage amplifier of this type is approximately the 4th power of the amplification per stage as shown in figure 7. The step-up in

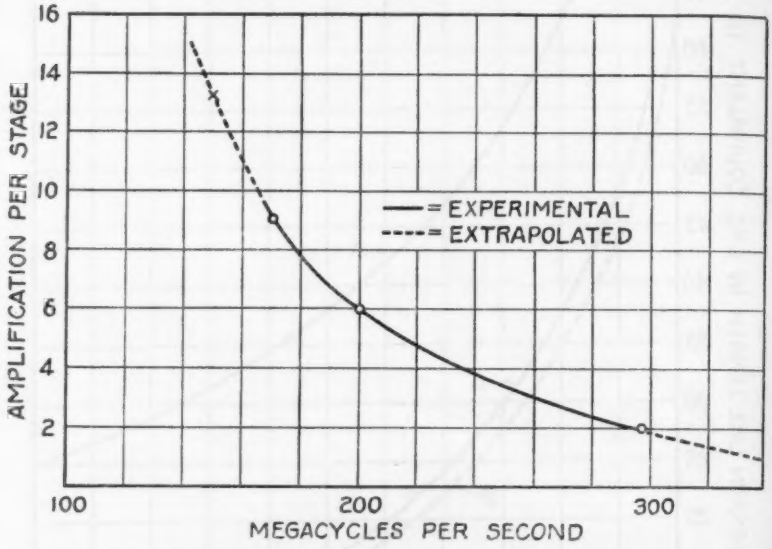

FIGURE 7.—*Amplification per stage for the concentric line tuned receiver at frequencies from 150* Mc/s *to 300* Mc/s.

the antenna coupling impedance is approximately 1.5 to 1. The effective amplification is further increased by the nonlinear operation of the detector. By actual measurement the over-all effective amplification of the amplifier and detector at 300 Mc/s is 125 (approximately 42 db), at 200 it is 93,000 (approximately 100 db), and at 170 Mc/s it is 1,060,000 (approximately 120 db). This over-all gain should be multiplied by the detector conversion efficiency and by the amplification on the intermediate modulating frequency in the first detector and in the broadcast receiver in order to determine the over-all amplification of the complete receiving set-up.

Measurements were made on a line with a ratio of inner and outer line diameters of 3.60 instead of 9.20. While this ratio should have given more gain due to a greater Q, measurements did not show this effect at 300 Mc/s. This was probably due to the predominance of lead and electron-tube resistance over the concentric line equivalent series resistance. The smaller ratio of diameters tuned to resonance with the line 3.5 cm longer than for the 9.2 ratio line. This was to be expected according to theory.

3. THIRD HARMONIC RESPONSE

A transmission line tuned to a certain fundamental frequency will also respond to a frequency near the third harmonic of this fundamental, as well as to other odd harmonics. This is due to the fact that the half-wave length section of a three-quarter-wave length line remains fixed at its full half-wave value, the variations due to the shunting capacitance occurring in the initial quarter-wave section. Thus for example the length of line for tuning to 300 Mc/s, as actually obtained by measurement, is 6.5 cm as shown by curve B, fig. 6. A half-wave length line for 300 Mc/s is 50 cm, therefore the length of line tuned to some fundamental frequency for which 300 Mc/s is an interfering third harmonic frequency is 50+6.5 or 56.5 cm. From

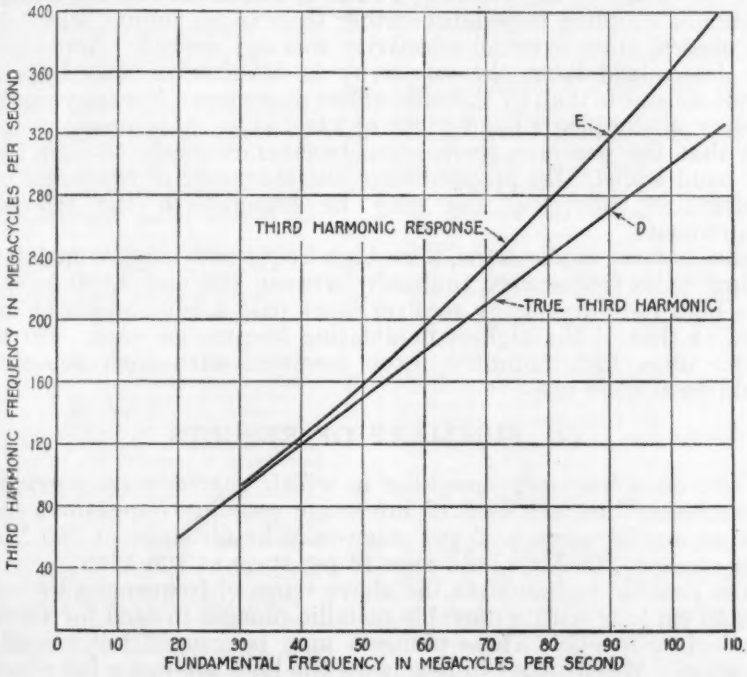

FIGURE 8.—*Deviation between the third harmonic response frequencies and the true third harmonic frequencies.*

graph B (fig. 6) the fundamental frequency to which the line (56.5 cm long) is tuned, is 86 Mc/s. In other words, when tuned to a fundamental of 86 Mc/s, a frequency of 300 Mc/s would be received (if present) and not 258 Mc/s, the actual third harmonic frequency.

In figure 8, curve E shows how this third harmonic response frequency differs from the true third harmonic for various fundamental frequencies. The question of interference which may be caused by this third harmonic response effect when using transmission lines as interstage coupling impedances is not as serious as one might expect due to the rapid decrease in amplification per stage at the higher (third harmonic) frequencies.

Thus, for example, from figure 7 the amplification per stage at 100 Mc/s is probably well over 16. From curve E, figure 8, the third

harmonic response frequency for this fundamental is 360 kc/s. The amplification per stage at this frequency as shown from figure 7 is probably less than 1, a considerable difference when the over-all gain is considered. For fundamental frequencies higher than 100 Mc/s the receiver becomes even less responsive to the third harmonics. A receiver of this type for use above 100 Mc/s should require a very strong third harmonic interfering signal as compared to the fundamental before any interference would be noted. Furthermore the gain for a three-quarter wave length line would be considerably less than for a $\lambda/4$ wave line due to increased attenuation along the longer line.

4. SHARPNESS OF RESONANCE

In the design of this receiver, a ratio of diameters corresponding to maximum coupling impedance rather than to maximum selectivity, was chosen, since extreme selectivity was not desired. Actually, as was determined later, the selectivity is determined more by other circuit constants than by the ratio of line diameters. For television the receiver should pass a band width of 2,000 kc/s. Measurements indicate that the present experimental receiver responds to over twice this band width. By proper design the sharpness of resonance of a receiver for television use may be brought to the television requirements.

Since in most applications, ultra high frequencies may be modulated by low radio frequencies, probably between 550 and 3,000 kc/s, an ultra high radio-frequency receiver must pass a band width at least equal to that of the highest modulating frequencies used. For this service ultra high radio-frequency receivers with high selectivity would be of little use.

VII. SUMMARY OF RESULTS

Tests on a four-stage amplifier in which quarter-wave concentric transmission lines are used as interstage coupling impedances show that an amplification of 2 per stage may be obtained at 300 Mc/s, 6 per stage at 200 Mc/s, and over 16 per stage at 100 Mc/s.

It is possible to tune over the above range of frequencies by using lines 50 cm long with a movable metallic plunger in each for varying its effective length. These plungers may be ganged for unicontrol operation. When tuned to resonance the lines are not a full quarter wave long but 27% of this amount at 300 Mc/s, 50% at 171 Mc/s, and 58.7% at 100 Mc/s. By running the direct current plate supply lead down through the center of the inner concentric line it is possible to use one in place of two concentric lines between each stage and the next.

The possibility of interference in this receiver due to third harmonic response is probably negligible as the receiver is insensitive above 360 Mc/s.

I am indebted to H. Diamond for advice during the progress of this work and for the theoretical analysis of many of the data obtained.

Acknowledgment is also due L. L. Hughes for the construction of the receiver and for valuable suggestions on the mechanical design.

WASHINGTON, October 14, 1935.

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